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(54) Title: PROCESS FOR PREPARING A POLYMER HAVING PERFLUOROCYCLOBUTANE RINGS AND POLYMERS CONTAINING PERFLUOROCYCLOBUTANE RINGS

(57) Abstract

The present invention includes a process for preparing a polymer having perfluorocyclobutane rings by the steps of (a) contacting monomers having at least two dimerizable perfluorovinyl groups; and (b) exposing the monomers to heat such time that a polymer containing perfluorocyclobutane rings is formed. The present invention includes polymers having a backbone comprising hydrocarbyl groups, perfluorocyclobutane rings and non-carbon atoms and polymers of at least 10,000 molecular weight having repeating units $[O-(CFR)_n-O\text{-perfluorocyclobutane}]$. The present invention also includes crosslinked polymers having perfluorocyclobutane rings and thermal processes to prepare such crosslinked polymers. Crosslinked polymers have tensile strength and other physical properties enhanced over the properties of the corresponding linear polymer.

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PROCESS FOR PREPARING A POLYMER HAVING
PERFLUOROCYCLOBUTANE RINGS AND POLYMERS CONTAINING
PERFLUOROCYCLOBUTANE RINGS

This invention relates to polymerizations of
perfluorovinyl compounds and to compositions containing
more than one perfluorocyclobutane ring, more
5 particularly to polymeric compositions containing more
than one perfluorocyclobutane ring.

It has long been recognized that perfluorovinyl
10 compounds having more carbon atoms than
tetrafluoroethylene are very difficult to polymerize
into aliphatic chains. Such difficulties are discussed,
for instance, in U.S. Patent Nos. 2,848,504 and
2,958,685; and in J. Polymer Science, Part 1-A,
15 pp. 481-492 (1952) and vol. 6, pp 711-717 (1968).

Dimerization of certain perfluorovinyl
compounds has been reported and is discussed, for
instance, in Chambers, Fluorine in Organic Chemistry,
20 John Wiley, New York, 1973, pp. 173-191; S. Patai, The
Chemistry of Alkenes, Wiley Interscience Publishers,
1964, p. 779; M. Hudlicky, Chemistry of Organic Fluorine
Compounds, 2nd ed., Halsted Press (John Wiley and Sons),
25 1972, p. 450; and Tarrant ed., Fluorine Chemistry

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Reviews, Vol. 2, Marcel Dekker, 1968 pp. 1-52. In general, the dimerizations are easily sterically hindered and have not been used to prepare long chain molecules. U.S. Patent No. 3,316,312 describes dimerization linking two molecules of such compounds as perfluoropropylene and perfluoropentene-1, and speculates that the reaction could be used for perfluoroalkyl perfluorovinyl compounds wherein the alkyl radical has 1 to 20, "or even a higher number" of carbon atoms.

Such dimerization has not previously been reported to produce compounds having more than one perfluorocyclobutane ring. In fact, few compounds having multiple perfluorinated four carbon-rings have been reported. U.S. Patent No. 3,303,145 discloses a number of polyethers formed from cyclic fluorocarbon epoxides, which polymers can have perfluorocyclobutane rings separated by oxygen atoms. The polymers are said to have good thermal stability and chemical inertness as well as dielectric properties. Use as solvents, heat-transfer media and lubricants as well as insulators in the form of films and moldings is suggested. U.S. Patent No. 3,682,876 discloses polyperfluorocyclobutene and halogen terminated polyperfluorocyclobutadienes. The solid polyperfluorocyclobutadienes are reported to be thermally stable, chemically inert and useful as coatings, ablatives, gaskets, bearings, potting compounds and sealants. U.S. Patent No. 3,900,380 discloses polymers prepared by coupling certain perfluoroalkyl or perfluoroalkyl ether chains with iodine terminated perfluorocyclobutanes to prepare polymers having double bonds suitable for cross linking. The liquids are reported to be useful as hydraulic

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fluids, and the solids as gaskets and ablatives. Certain polymers containing radical-initiated rings, assumed for steric reasons to be four-membered rings are reported by Brown et al. in J. Polymer Sci: Part A vol. 3, pp 1641-1660 (1965) and vol. 4, pp 131-140 (1966). None of these reported polymers having perfluorocyclobutane rings is formed by thermal reaction of perfluorovinyl groups. Also, none has aromatic structure.

10 In one aspect the present invention is a process for preparing a polymer having perfluorocyclobutane rings comprising the steps of:
15 (a) contacting monomers having at least two dimerizable perfluorovinyl groups; and

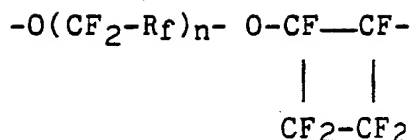
(b) exposing the monomers to heat such that a polymer containing perfluorocyclobutane rings is formed.

20 In another aspect the present invention includes polymers formed by the above process.

25 In another aspect the present invention is a polymer having a backbone comprising a hydrocarbyl group, perfluorocyclobutane rings and at least one non-carbon atom.

30 In yet another aspect, the present invention is a polymer having repeating units represented by the following formula:

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wherein the polymer has an average molecular weight of at least about 10,000.

10 In still another aspect, the present invention is a process for preparing a crosslinked polymer having perfluorocyclobutane rings comprising the steps of:

- 15 (a) contacting monomers having two dimerizable perfluorovinyl groups;
- (b) exposing the monomers to heat such that a polymer containing perfluorocyclobutane rings is formed; and
- 20 (c) exposing the polymer to a crosslinking initiating means such that crosslinking occurs.

25 In still another aspect, the present invention is a crosslinked polymer produced by that the above process.

The crosslinked polymers are advantageously elastomeric in the range from their glass transition temperatures to the temperatures at which degradation is observed, which is generally on the order of 400°C to 450°C. Compared to their thermoplastic counterparts, the crosslinked polymers exhibit enhanced solvent resistance and increased mechanical strength, without

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loss of advantageous electrical properties, such as low dielectric constant and dissipation factor.

Polymers of the invention are formed by thermal reaction of monomers having at least two dimerizable perfluorovinyl groups such that perfluorocyclobutane groups are formed. A dimerizable perfluorovinyl group is a perfluorovinyl group which reacts with another such group to form a perfluorocyclobutane ring. Thus, resulting polymers have at least two perfluorocyclobutane groups, in particular sufficient perfluorocyclobutane groups to achieve physical and electrical properties desired for specific uses of the polymers. The term "polymer" is used herein to refer to any compound having at least two perfluorocyclobutane groups formed from perfluorovinyl groups, and includes oligomers which have from 2 to 100 repeating units and preferably have a molecular weight of from 300 to 30,000. It is within the scope of the present invention to form lower molecular weight oligomers useful as fluids or prepolymers and higher molecular weight polymers exhibiting general plastic properties. Within this scope and depending on the molecular structure connecting the perfluorocyclobutyl groups, the number of perfluorocyclobutane groups can vary from as few as two up to thousands. The process of forming polymers or oligomers by the process of the present invention is general and capable of forming products having wide ranges of utility. Physical and electrical properties of the resulting products are highly dependent on the choice of the molecular structure between the perfluorocyclobutane groups as well as the number of perfluorocyclobutane groups.

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The relative proportion by weight of the perfluorocyclobutane groups to the other molecular components of the resulting products can vary over a wide range of from 12 to 1 to 0.01 to 1, preferably from 5 to 1 to 0.02 to 1 and most preferably from 2 to 1 to 0.03 to 1. High proportions of perfluorocyclobutane groups are desirable for instance, when fluorocarbon character such as low dielectric constant is beneficial in the products. Exemplary of such products are low dielectric fluids and lubricants. Medium ranges of ratios of weights of perfluorocyclobutane groups to other molecular structures of 2 to 1 to 1 to 4 are desirable, for instance, when higher physical strength and relatively lower dielectric constants (for example, relative to conventional engineering thermoplastics) are desired, for example, in low dielectric plastics. These relatively low dielectric plastics are particularly preferred and are preferably achieved by using aromatic compounds substituted with trifluorovinyl groups, most preferably, with trifluorovinyl ether groups. Very low proportions of the perfluorocyclobutane groups result, for instance, when low molecular weight oligomers (for example, in the range of 1000 to 20,000) are terminated by trifluorovinyl groups and then thermally dimerized to form higher molecular weight polymers.

Any monomer having at least two dimerizable perfluorovinyl groups is suitably used in the practice of the present invention. Whereas polyaddition of perfluorovinyl groups to form perfluoroaliphatic polymers (like polytetrafluoroethylene), not generally having perfluorocyclobutane groups, takes place in the presence of free radicals or free radical generating

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catalysts, dimerization to form perfluorocyclobutane groups takes place thermally.

In the thermal polymerization of
5 diperfluorovinyl compounds, substantially linear
polymers having little branching are believed to be
formed. In the practice of one embodiment of the
present invention, certain of these substantially linear
10 polymers are crosslinked. Crosslinking involves
chemical reactions that interconnect polymer molecules.
As these reactions proceed, a polymer network is formed.
Early in a crosslinking process, there are molecules
having a wide variety of molecular weights; molecular
weight increases with increasing extent of crosslinking.
15 At a point in the progress of crosslinking, the gel
point is reached. This point is defined as the point
when there is sufficient crosslinking that the polymer
is no longer soluble in a solvent for the corresponding
uncrosslinked linear polymer. Rather, the polymer
20 swells in the solvent. Theoretically, either the weight
average molecular weight diverges to infinity in an
infinite sample, or a first macromolecular cluster grows
to be on the order of the sample size when the sample is
finite. At the gel point, the polymer system loses its
25 solubility and a steady-shear viscosity approaches
infinity. In the practice of the present invention at
least two types of crosslinking are observed. A first
type of crosslinking involves the use of monomers having
30 at least three perfluorovinyl groups such crosslinking
is referred to herein as "polyfunctional crosslinking."
A second type of crosslinking is observed when certain
types of monomers are used, and because it is believed
that this second type of crosslinking involves certain
aromatic structures in the backbone of the polymer, it

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is referred to herein as "backbone crosslinking." In the case of backbone crosslinking, a decrease in percent elongation as measured by the procedure of ASTM D882-83 is also observed. Preferably, the decrease in percent elongation is at least about 10 percent, more preferably at least about 20 percent of the percent elongation. At the gel point, there are still unattached polymer molecules within a polymer network system. As these molecules are crosslinked into the network, stiffness increases and the mechanical strength of the polymer (for example, as measured by the procedures of ASTM D882-83 and ASTM D790-81) is enhanced. The viscosity also continues to increase. The gel point at a temperature can be determined rheologically by the process of H. H. Winter et al. in J. Rheology, 30(2), 367-382 (1986) and 31(8), 683-697, (1987); and Macromolecules, 22, 411-414, (1989). As measured by the procedure taught by Winters, crosslinked polymers of this invention preferably have gel points within about two hours at about 360°C, more preferably in less than about two hours at 320°C, most preferably in less than about two hours at 280°C. Measurements at temperatures below about 320°C are more indicative of a preferred crosslinking because crosslinking at such temperatures is accompanied by thermal decomposition.

Before crosslinking, solid polymers of the invention are generally thermoplastic. Viscosity of either a melt or solution of the polymer increases as crosslinking occurs until the gel point and resulting unsolubility is reached. Backbone crosslinked polymers are preferably elastomeric, that is, the polymer can generally regain its shape after deformation. That deformation is indicated by elongation measurements

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greater than about 100 percent at temperatures above the glass transition temperature (T_g) of the polymer.

5 Backbone crosslinked polymers preferably retain their elastomeric properties at temperatures of from their glass transition temperatures to the temperatures at which they are observed to degrade, preferably about 400°C. The glass transition temperature varies with the composition of the polymer.

10 Backbone crosslinking also increases a polymer's tensile strength as measured by the procedures of ASTM D882-83. The increase is preferably up to 1000 percent, more preferably from 10 percent to 500 percent, most preferably of from 10 percent to 15 100 percent increase. Also the polymer's tensile and flexural modulus as measured by the procedures of ASTM D882-83 and ASTM D790-81, respectively, also increases, preferably up to 1000 percent, more preferably of from 10 percent to 500 percent, most preferably of from 20 10 percent to 100 percent. Additionally, the fluorine-containing structures of such crosslinked polymers preferably retain relatively low dielectric constants.

25 Although any monomer having two dimerizable perfluorovinyl groups and which is crosslinkable is suitably used for backbone crosslinking, backbone crosslinked polymers of the invention are preferably prepared from monomers having two perfluorovinyl groups 30 separated by at least one hydrocarbyl group having at least one carbon atom between the perfluorovinyl groups.

When a perfluorovinyl group is dimerizable, dimerization is preferably favored over other thermal reactions either kinetically or in equilibrium. In

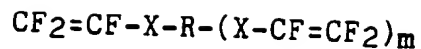
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perfluorobutadiene, isomerization and formation of perfluorocyclobutane rings is favored; it is, therefore, preferable in the practice of the present invention that the perfluorovinyl groups on a monomer used in the practice of the present invention be separated by at least one atom or group of atoms, which group does not facilitate isomerization. The atom or group of atoms preferably includes at least one carbon atom, more preferably at least one carbon atom in an, optionally substituted, hydrocarbyl group, that is a group containing at least one carbon-hydrogen bond, for instance, a methylene group, a phenylene group, a phenylene ether group or a pyridinyl group.

Furthermore, when the perfluorovinyl groups are attached to aliphatic carbons or separated from aliphatic carbons by single atoms such as oxygen, the perfluorovinyl groups are preferably primary or secondary because tertiary perfluorovinyl groups are generally sterically hindered with respect to formation of perfluorocyclobutane rings, more preferably the perfluorovinyl groups are primary because secondary perfluorovinyl groups tend to rearrange. Preferably, to avoid rearrangement and facilitate polymer formation and crosslinking the monomers have structures such that resulting polymers have hydrocarbyl groups (preferably aromatic rings), perfluorocyclobutane rings and at least one non-carbon atom such as oxygen, silicon, boron, phosphorus, nitrogen, selenium, tellurium and/or sulfur atom (each optionally substituted) in the backbones.

The monomers preferably have a structure represented by the following Formula I:

Formula I



wherein R represents an, optionally inertly substituted
5 group; each X is independently a bond or any group which
links R and a perfluorovinyl group (hereinafter linking
structures), said structures being inert; $m+1$ is the
number of $-\text{X}-\text{CF}=\text{CF}_2$ units. Advantageously, m is an
integer of from 1 to 3, preferably from 1 to 2. While
10 compounds represented by Formula I wherein m is one are
especially useful for forming linear polymers, compounds
wherein m is 2 or more particularly 2 or 3 are
especially useful for polyfunctional crosslinking. By
15 "inert" it is meant that the structures or substituents
do not react undesirably with perfluorovinyl groups or
interfere undesirably with polymerization
(perfluorocyclobutane formation) of the monomers.

20 Linking structures X are each independently a
linking structure such as a bond, an oxygen atom,
carboxylic and thiocarboxylic ester groups, other sulfur
containing structures, perfluoroalkylene,
25 perfluoroalkylene ether, alkylene, acetylene, phosphorus
containing groups such as phosphines, carbonyl and
thiocarbonyl groups; seleno; telluro; nitrido; silicon-
containing groups such as silanediyl, trisilanediyl
tetrasilanetetrayl, siloxanediyl, disiloxanediyl,
30 trisiloxyl, trisilazanyl, or silylthio groups; boron-
containing groups such as boranediyl or methylboranediyl
groups; a combination thereof, or any other group which
is inert, which molecularly links R to a perfluorovinyl
group, and which provides a molecular structure in which
the perfluorovinyl group is sufficiently reactive to

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form a perfluorocyclobutane ring. For instance, X is preferably other than a perfluoroalkylene group because perfluorovinyl groups attached to perfluoroalkylene groups generally require temperatures greater than about 300°C to dimerize and are subject to isomerization.

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It is preferred that at least one of X is not a bond. More preferably, X is independently selected from the group consisting of groups having at least one non-carbon atom between the perfluorovinyl groups and R, such as groups containing oxygen, sulfur, selenium atoms, tellurium atoms, silicon, boron, phosphorus or nitrogen between R and the perfluorovinyl group, for example, oxygen atoms, sulfur atoms, (thio) carboxylic ester groups, phosphines, (thio) carbonyl groups, seleno, telluro, silanediyl, trisilanediyl, trisilazanyl or silylthio, boranediyl groups. Preferred groups have S, O, Si, N or P, more preferably S, O, or Si between R and the perfluorovinyl group, such as carbonyl, thiocarbonyl, sulfone, sulfoxy, silanediyl, amines (optionally inertly substituted), oxygen or sulfur atoms. Most preferably there is a single atom other than carbon between R and each perfluorovinyl group; even more preferably the single atom is oxygen or sulfur, among those groups preferably an ether or sulfide linkage, because monomers having such linking structures advantageously form perfluorocyclobutane groups at lower temperatures than are needed with such groups as perfluoroalkyl groups and are more stable than monomers where the perfluorovinyl group is attached directly to R, particularly when R is aromatic. Monomers having such linking structures are also relatively easily prepared.

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R is suitably any inert molecular structure, preferably a molecular structure which facilitates formation of perfluorocyclobutane rings and/or polyfunctional crosslinking and/or imparts desirable physical properties to polymers or oligomers prepared from the monomers. For the purpose of imparting desirable physical properties to polymers, R preferably contains at least one carbon atom. Preferably, the carbon atom is in the molecular chain between X's because monomers having at least one carbon atom between X's when X is other than a bond, tend to have desirable stability and to produce polymers having desirable physical properties. Alternatively, the carbon atom is in a side chain; for instance, -R- can be -N(CH₃)-, -N(CH₂CH₃)-, -P(CH₃)- or -P(CH₂CH₃)-. The carbon atoms(s) in R are suitably in aliphatic, cycloaliphatic, aromatic, heterocyclic groups or combinations thereof. Additionally, R optionally contains groups or has substituents which are inert, that is which do not undesirably interfere with the formation of perfluorocyclobutane rings from perfluorovinyl groups. Inert substituents include ether, carbonyl, ester, tertiary amide, carbonate, sulfide, sulfoxide, sulfone, nitrile, alkyl phosphonate, tertiary amine, alkyl phosphate, alkyl silyl, chlorine, bromine, fluorine, alkyl, arylalkyl, alkylaryl, cycloalkyl, aromatic, heterocyclic, alkoxyl and aryloxy groups, which inert substituents are suitably in any position, for instance, in a polymer backbone between X's and/or appended to such a backbone. Carbon-containing inert substituents on R preferably contain from 1 to 50, more preferably from 1 to 12 carbon atoms because of the stability and ease of working with monomers of lower molecular weight. R, including inert substituents preferably has a

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molécular weight (MW) of from 14 to 20,000, more preferably from 75 to 15,000 and most preferably from 75 to 5,000. These ranges include monomeric and oligomeric R groups. In the case of monomers which are other than oligomeric, R preferably has from 1 to 50, more preferably from 6 to 50, carbon atoms because molecular weights above this reduce the contribution to properties made by the fluorine-containing substituents when R is alkyl or aromatic hydrocarbon. As previously discussed, the nature of R as well as the perfluorocyclobutane content of the polymers can vary broadly according to the type of products desired.

Preferably, for polymers having good plastic properties such as tensile strength and flexibility, at least one carbon atom of R is in the molecular chain between X's and is part of an aromatic nucleus. Aromatic groups are desirable because of improved physical properties of the polymers and ease of manufacture of the monomers. For both ease of manufacture of the monomer and monomer stability, when R is aromatic, each X is preferably independently sulfur or oxygen. The aromatic group can be any molecular structure having aromatic character, advantageously having at least one six-membered aromatic ring, suitably having any number of such six-membered rings fused together or connected by bonds or linking structures. R preferably has from 1 to 50 such rings, more preferably from 1 to 10 rings, more preferably containing from 6 to 25 carbon atoms, most preferably R has at least 2 to 4 aromatic rings to impart properties such as hardness and/or stiffness to a polymer. The aromatic fragment is suitably unsubstituted or inertly substituted. Inert substituents on an aromatic R include, for instance, the

inert substituents listed for R generally. Exemplary aromatic molecular fragments include, for instance, perchlorophenylene, phenylene, biphenylene, naphthylene, dichlorophenylene, nitrophenylene, p,p'(2,2-diphenylene propane) $[-C_6H_4-C(CH_3)_2-C_6H_4-]$; p,p'-(2,2-diphenylene-1,1,1,3,3,3 hexafluoropropane) $[-C_6H_4-C(CF_3)_2-C_6H_4-]$, preferably biphenylene; phenylene; 9,9'-diphenylfluorene, oxydiphenylene; thiodiphenylene; 1,1,1-triphenyleneethane; 1,3,5-triphenylenebenzene; 1,3,4-(2-phenylene-2-propyl)benzene; 1,1,1-triphenylenemethane; 1,1,2,2-tetraphenylene-1,2-diphenylethane; bis(1,1-diphenyleneethyl)benzene; 1-(2-phenylene-2-propyl)-4-(1,1-diphenyleneethyl)benzene; 2,2-diphenylene propane; 2,2'-diphenylene, 1,1,1,3,3,3-hexafluoropropane; 1,1-diphenylene-1-phenylethane; naphthalene; and anthracene. Molecular weights of aromatic ring containing polymers are preferably at least about 10,000. Such aromatic groups are preferably present because they generally impart high temperature glass transition properties (T_g) and good mechanical strength (for example, as measured by differential scanning calorimetry (DSC) and tensile/flexural tests) to the polymer.

For the purpose of facilitating backbone crosslinking, more preferably, R is a group which reacts with perfluorovinyl groups residual in a substantially linear polymer to form a crosslinked or branched molecular structure. The reaction of R with the perfluorovinyl groups is suitably initiated by heat, free radicals, wave energy, or any other crosslinking initiating means, but preferably by heat. Most preferably R includes a structure having two double, triple or aromatic bonds (hereafter multiple bonds)

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separated by a single bond. Such structures are recognized in the art as latent dienes. Preferably the latent dienes are suitable for reactions of the Diels-Alder type, more preferably suitable for such reactions with perfluorovinyl groups in the monomers, most
5 preferably suitable for such reactions with perfluorovinyl ether groups under conditions used for crosslinking. The single bond is preferably a carbon to carbon single bond. Each of the multiple bonds is
10 independently suitably a multiple bond between any two atoms, preferably between a carbon atom and any other atom (for example, $-C=O$, $-C=C-$, $-C\equiv N$), more preferably a carbon to carbon bond. Exemplary of preferred R
15 9,9'-diphenylfluorene, fluorene, cyclopentadienylene, furan and anthracene.

Even though Diels-Alder reactions of perfluorovinyl groups are rare (See D. D. Coffman, et
20 al., J. Am. Chem. Soc., 71, 490-496 (1949); E. T. McBee, et al., J. Am. Chem. Soc., 77, 915-917 (1955); J. J. Drysdale, et al., J. Am. Chem. Soc., 80, 3672-3675 (1958)), monomers capable of such reactions are observed
25 to give backbone crosslinked polymers having gel points at temperatures generally lower than similar polymers formed from monomers wherein double bonds are separated by more than one single bond.

30 Most preferably, at least one aromatic carbon atom of R is bonded directly to X, most preferably aromatic carbon atoms of R are bonded directly to each X because perfluorovinyl groups bonded to X, said X being

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bonded to aromatic groups are generally more reactive in forming perfluorocyclobutane rings.

Some specific combinations of X and R are especially preferred: when R is aromatic, at least one X is preferably other than a bond, more preferably neither X is a bond, because attachment of perfluorovinyl groups directly to aromatic R renders the perfluorovinyl groups more thermally and oxidatively unstable than when said groups are attached, for instance to oxygen or sulfur. When R is a perfluoroalkyl group or a perfluoroalkylether group, at least one X is preferably other than a bond, most preferably no X is a bond or a perfluoroalkyl group, because perfluorovinyl groups linked directly to perfluoroalkyl groups require temperature in excess of about 300°C to dimerize and are subject to isomerization.

Monomers useful in the practice of the present invention are suitably prepared by any method which links molecular structures having perfluorovinyl groups to other molecular structures or which forms perfluorovinyl groups.

Perfluorovinyl groups are formed, for instance by elimination of halogens from terminal dihalotrifluoroethyl groups. Halogens such as bromine or iodine may be eliminated, for instance, using metallic reactants as illustrated by Cohen's synthesis of trifluorostyrene by the reaction of zinc with dichlorotrifluoroethylbenzene in absolute ethanol (J. Am. Chem. Soc., 71, 3439, (1949)). Additionally, pentafluoroethyl (substituted) phenyl ethers can be reacted with certain phosphorus compounds to form

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perfluorovinyl ethers as reported by Kawaguchi et al. in Japanese Kokai 77 89,603. Structures suitable for elimination of halogens to form perfluorovinyl groups are prepared, for instance, by processes such as those taught in Rico et al. U.S. Patent No. 4,377,711 and Carl
5 et al. in U.S. Patent No. 4,423,249. Additionally perfluorovinyl groups are formed by decarboxylation of perfluorocarboxylic acids with concomitant loss of hydrogen fluoride, as taught by R.N. Griffin and M.I. Bro, J. Org. Chem., 25, 1068 (1960), and also by T.S.
10 Reid, G.H. Smith, and W.H. Pearlson, in U.S. Patent No. 2,746,997. Electrochemical elimination of halogens from certain substituted alkyl-1,2-dihalo-1,2,2-trifluoroethyl ethers according to the procedures taught
15 in European Patent document EP 293,856 is also useful for forming perfluorovinyl compounds.

Tetrafluoroethylene and chlorotrifluoroethylene are reacted with suitable compounds, for instance, by
20 procedures taught by Prober in J. Amer. Chem. Soc., 75, 968 (1953); by Plumer et al. in U.S. Office Saline Water, Res. Develop. Prog. Rep. #481, 1969; by Dixon in J. Org. Chem., 21, 400 (1956); and by Wall et al. in
25 U.S. Patent No. 3,277,068.

Linking of molecular structures containing perfluorovinyl groups to other molecular structures is illustrated by reaction of (trifluorovinyl)trimethyltin
30 aryl iodides in the presence of palladium complexes, as taught by R.S. Sorokina, et al. in Zh. Org. Khim., 18, 2458, (1982); by the reaction of trifluorovinyl zinc reagents with certain substituted phenyl iodides as taught by R.S. Sorokina et al. in Izv. Akad. Nauk SSSR, Ser. Khim., 1647, (1985); and Heinze and Burton in

J. Fluorine Chem., 31, 115, (1986), and J. Org. Chem.,
53, 2714, (1988).

Preferred monomers are preferably prepared by
the process taught in copending U. S. Patent Application
5 Serial No. 364,665, filed June 9, 1989.

An exemplary method of preparing a tris-
perfluorovinyl ether (exemplary of monomers having three
perfluorovinyl groups) is illustrated by a process
10 having the following steps:

(A) A trihydroxy compound such as 1,1,1-
tris(4-hydroxyphenyl)ethane is converted to its sodium
15 or potassium salt in a solvent such as a methanol/water
mixture. The methanol or another solvent for the
trihydroxy compound is used when, as in the case of
1,1,1-tris(4-hydroxyphenyl)ethane, the compound is not
20 water soluble. Sufficient alcohol is used to keep the
trihydroxy compound in solution; in the case of 1,1,1-
tris(4-hydroxyphenyl)ethane from about 20 to about
50 volume percent based on total volume of alcohol and
water is convenient. Salt formation occurs conveniently
25 at from about 0 °C to about 60 °C at atmospheric
pressure, preferably under a nitrogen atmosphere to
avoid oxidation.

(B) The methanol is removed under reduced
30 pressure at any convenient temperature and pressure with
replacement of water as it is lost.

(C) The salt is dried and powdered for
example, in a drum dryer.

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(D) The salt is slurried in a polar, aprotic solvent suitable for achieving reaction such as DMSO (dimethyl sulfoxide), ether diglyme, DMF (dimethyl formamide) HMPA (hexamethylphosphoramide) diglyme, 5 tetraglyme or glyme and an aprotic azeotropic medium such as toluene or chlorobenzene in a solvent to azeotrope medium ratio of from 10 to 1 to 1.5 to 1 and dried by the azeotropic removal of water.

10 (E) About half of the toluene is removed, for example, by distillation and the mixture is cooled below about 50°C, preferably below about 20°C.

(F) A dihalotetrafluoroethane such as 1,2- 15 Dibromotetrafluoroethane is added to form a mixture as the reaction temperature is controlled at a temperature suitable for the reaction to occur substantially without the side reaction of ring bromination halogenation; in 20 the case of 1,1,1-tris(4-hydroxyphenyl)ethane preferably below about 20°C initially. The mixture is stirred at 18°C to 25°C for 36 hours.

(G) The mixture is poured into about an equal 25 volume of cold water, conveniently from about 0.5 to about 3 times the volume of the solution, and the product falls out as the lower layer. There is preferably sufficient cooling to offset the heat generated by admixing DMSO (or other solvent) and water. 30

(H) The product, a tris-bromide, is distilled, for example, at 190°C to 195°C/0.05 mm Hg. When tris-bromides are heat stable as observed in the case of 1,1,1-tris(4-(2-bromotrifluoroethoxy)phenyl)ethane, the degree of vacuum is selected to give a convenient

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boiling point. Such selection is within the skill in the art.

(I) The tris-bromide is used directly or, if desired, in cases where the tris-bromide is a solid it may be dissolved for ease of addition in a polar, aprotic solvent such as diglyme, tetraglyme or glyme and added to a hot (for example 120°C) mixture of the same solvent and granular zinc to form the tris-perfluorovinyl ether (TVE). Alternatively, the tris-bromide can be added to a hot (for example 120°C) mixture of, for example, diglyme and granular zinc as a melt without dilution if heated above its melting point, for example to about 120°C in the case of 1,1,1-tris(4-(2-bromotrifluoroethoxy)phenyl)ethane. Temperatures above about 125°C are preferably avoided to avoid dimerization of perfluorovinyl groups.

(J) The TVE is isolated by removing the zinc salts for example by centrifugation, evaporating the diglyme under reduced pressure, diluting the TVE with a, preferably low boiling, solvent such as hexane, and flushing the solution through a pad of neutral alumina. Alternatively, the zinc salts are removed by filtration and the TVE distilled under vacuum, for example in two stages, the first to remove solvent and the second to purify the TVE. Preferably, temperatures above about 110°C are avoided to avoid dimerization of perfluorovinyl groups. Especially when a very pure product is desired, these methods of purification are suitably combined.

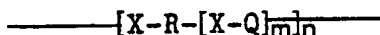
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K) The hexane, if used, is removed from the TVE by evaporation under reduced pressure.

Alternatively, the TVE is isolated by removing the zinc salts by filtration, evaporating the diglyme under reduced pressure, diluting the TVE with hexane and purifying by countercurrent extraction with polar organic materials such as acetonitrile or DMSO. The pure TVE in hexane is then flushed through a pad of alumina and isolated by concentration under reduced pressure.

Polymers produced from the preferred monomers preferably have a formula represented by the following Formula II:

Formula II



wherein R, X, and m, are defined above, Q is a perfluorocyclobutane group; and n is an integer representing the number of repeating units, which is preferably from 2 to 100,000. More preferably from 2 to 10,000, most preferably from 3 to 5,000. More preferably m is one or two. Formula II is generalized; when m is greater than one, some of the -X- Q structures represent branching and/or crosslinking.

The monomers are heated to a temperature and for a time sufficient to form perfluorocyclobutane rings. Temperatures suitable for forming

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perfluorocyclobutane rings differ with the structure of the monomer. In general, temperatures above about 40°C are suitable for formation of perfluorocyclobutane rings, preferably the temperature is above about 50°C, more preferably above about 100°C, because these temperatures result in formation of the rings at successively faster rates. Temperatures above about 450°C are preferably avoided because perfluorocyclobutane groups are generally thermally unstable above such temperatures. More preferably a temperature of from 105°C to 350°C, most preferably from 105°C to 250°C is used to produce the perfluorocyclobutane rings at a convenient rate. Within that range, a temperature of from 100°C to 230°C is generally most preferred for cyclization of perfluorovinyl aromatic or aliphatic ethers or sulfides, while a temperature of from 50°C to 80°C is needed to form perfluorocyclobutane groups when the perfluorovinyl group is attached directly to an aromatic ring. In the case of perfluoroalkylperfluorovinyl groups, however, temperature of at least about 300°C, preferably at least about 350°C, is generally required.

Preferably, especially when the perfluorovinyl compounds are capable of radical initiated addition polymerization, conditions conducive to free radical polymerization, for example, presence of oxygen, ozone, peroxygen compounds and other free radical generating compounds, are avoided so that the perfluorovinyl groups will dimerize into perfluorocyclobutane groups rather than undergoing addition polymerization. Compounds known in the art for stabilization against free radical polymerization are alternatively used. Similarly, especially when the perfluorovinyl groups are capable of

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addition polymerization in the presence of anions or cations, compounds which supply such anions or cations are avoided. For instance, fluoride ions (for example, from carbonyl fluorides) chloride, hydroxide and phenoxide are preferably avoided. To avoid such
5 compounds as carbonyl fluorides, oxidative conditions such as presence of oxygen, hypochlorite, dichromate and permanganate are preferably avoided because perfluorovinyl groups are known to oxidize to form
10 carbonyl fluorides. Perfluorovinyl compounds such as perfluorovinyl ethers, thioethers, sulfones and sulfoxides are relatively stable with regard to addition polymerization and oxidation; and, therefore, such precautions are generally unnecessary when such
15 perfluorovinyl compounds are used.

Monomers or admixtures thereof are suitably neat or, optionally, in admixture with other materials such as in solution, in emulsion, in dispersions or in
20 any other form in which monomer molecules can be contacted with one another to form a polymer. Liquid admixtures are advantageous for maintaining contact between monomer molecules such that higher molecular
25 weight polymers are formed. This is particularly useful when linear thermoplastic polymers are the products. Neat polymerization is preferred when the monomers or prepolymers are formed in the final desired shape of the polymer article before final thermal treatment. This is
30 especially true when monomers having more than two perfluorovinyl groups are used in whole or in part to formed crosslinked, thermoset materials. Neat polymerizations or oligomerizations are also generally

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preferred to form relatively low molecular weight fluid products.

5 Suitable solvents are those which are inert to
the conditions encountered in the polymerization
reaction and include, for example, xylene, mesitylene
and perfluorotetradecahydrophenanthrene (MULTIFLUOR™
APF 215 commercially available from Air Products Corp.).
At atmospheric pressure, preferred solvents are those
10 which attain temperatures of 170°C to 250°C such as
dichlorobenzene, trichlorobenzene, diphenyl oxide and
perfluorotetradecahydrophenanthrene. Although solvents
such as 1,2-dichlorobenzene and 1,2,4-trichlorobenzene
give less satisfactory results such as discoloration of
15 the finished polymer, they are suitably used when their
disadvantages are tolerable in a final product. When a
solvent is used the concentration of monomers in solvent
is advantageously from 0.1 to 99.9 weight percent
preferably, from 10 to 90 percent by weight monomer.
20

 Polymerization or dimerization suitably takes
place at any pressure. Pressures are generally chosen
such that the monomers and any solvents and/or
25 dispersing media remain liquid at the temperatures used
for polymerization. When the monomers or other
materials evaporate at temperatures used, then it is
generally preferable to maintain a pressure at least
sufficient to maintain the materials liquid.
30 Additionally, the pressure for polymerization is any
pressure above the temperature at which a monomer boils
(or its vapor pressure is equal to that used in the
polymerization) at the temperature used for the

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polymerization preferably from 0.01 mmHg (1.33 Pa) to 20,000 psig (about 1,000,000 mmHg (1.3×10^5 kPa)).

Monomers having three or more dimerizable perfluorovinyl groups (hereinafter referred to as polyfunctional) are especially useful to form polymers having relatively high Tg believed to be due to polyfunctional crosslinking. From 0 to 100 percent by weight of such monomers are suitably used, preferably sufficient of the monomers having at least three perfluorovinyl groups to measurably increase the Tg of the polymer over that of a polymer of monomers having corresponding structures but with only two perfluorovinyl groups, more preferably at least about 0.05 mole percent, most preferably from 0.1 to 100 mole percent of such monomers is used. While use of lower proportions of polyfunctional monomer(s) produces, generally thermoplastic, polymers having crosslinking and corresponding properties of toughness and solvent resistance, use of sufficient polyfunctional monomers to form thermosetting polymers is useful to produce crosslinked polymers having higher Tg. The relative proportions of polyfunctional monomer which produce such polymers varies with the structure of the monomers. However, from 0.05 to 75 mole percent polyfunctional monomers used with monomers having 2 perfluorovinyl groups is sufficient to result in sufficient crosslinking in a thermoplastic polymer to reduce its solubility in a solvent. Thermoset polymers however are advantageously formed from monomer mixtures having from 75 to 100 mole percent, preferably from 85 to 100 mole percent of the polyfunctional monomers. For instance, a polymer of 1,1,1-tris(4-trifluoroethenyloxyphenyl)ethane which is 97 weight percent pure with the major impurity

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being 1,1-bis(4-trifluoroethenyloxyphenyl)-1-(4(1,1,2,2-tetrafluoroethoxy)phenyl)ethane is polymerized at 180°C to 240°C for 30 minutes and produces a colorless, transparent polymer having a Tg of 286°C.

- 5 While monomers of the invention are conveniently polymerized in a single stage polymerization, use of more than one stage is often advantageous particularly for polyfunctional monomers.
- 10 A first stage can advantageously be used to react some of the perfluorovinyl groups to reduce the exotherm frequently observed when large quantities of monomers, particularly of monomers having at least three perfluorovinyl groups are polymerized in a single stage.
- 15 A first stage is also useful to produce a monomer (or monomer mixture or solution) having increased viscosity and lower volatility than those of the initial monomer. A liquid or a solid of relatively lower melting point than that of a completely cured polymer is suitably
- 20 formed. Such a first stage of polymerization is conveniently carried out at temperatures of from 50°C to 400°C, preferably from 105°C to 250°C, more preferably from 120°C to 170°C. At least one later stage follows
- 25 the first stage and is preferably carried out at a higher temperature than the first to allow the polymerization to proceed toward completion. Such later stage(s) are conveniently carried out at temperatures from that sufficient to result in additional
- 30 polymerization up to the decomposition temperature of a resulting polymer, preferably from 100°C to 450°C, preferably from 120°C to 400°C, more preferably from 200°C to 375°C. Those skilled in the art will recognize that the first and later stages can represent more than one stage or can be carried out using two or more

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temperatures and that a series of stages or a continuum of temperatures are suitably used. In addition to these stages a postcure at relative high temperature such as from 200°C to 450°C is optionally used. The postcure is suitably for any duration sufficient to change physical properties and insufficient to decompose the polymer, preferably from 1 minute to 1 week, more preferably at high temperatures such as from 240°C to 450°C for duration of from 1 minute to 24 hours. Stages of polymerization are conveniently run under conditions previously described for polymerization of the monomers. When a solvent is used in an early stage, and it is desirable to avoid bubbles that may occur as a solvent is driven off, advantageously the solvent is removed before or during a later stage.

In a preferred embodiment of the present invention, conditions suitable for all or part of the dimerization can occur in a polymer shaping apparatus, for instance, an extruder, injection mold or compression mold. This embodiment of the present invention is particularly useful when materials containing perfluorovinyl groups, for instance, monomers, oligomers or polymers, have a viscosity suitable for introducing into the polymer shaping apparatus and the material resulting from the formation of perfluorocyclobutane groups in the apparatus has a higher viscosity or is solid, which is less suitable for introduction into the apparatus. More specifically, a perfluorovinyl containing oligomer or relatively lower molecular weight polymer, including the result of partial dimerization of perfluorovinyl groups is introduced into a shaping apparatus wherein it is heated sufficiently for formation of sufficient perfluorocyclobutane rings to

form a solid polymer. This technique is particularly useful when applied to oligomers of materials that would be difficult to fabricate as high molecular weight polymers, but where the properties of the higher molecular weight polymers are desired.

5

One such preferred embodiment of the present invention suitable for, but not limited to, formation of perfluorocyclobutane rings in a shaping apparatus involves forming trifluorovinyl terminated relatively low molecular weight (for example, from 300 to 30,000, preferably from 1,000 to 20,000, more preferably from 1,000 to 5,000) oligomers or polymers, that have a low viscosity relative to their higher molecular weight counterparts. Suitably low molecular weight polymers of the present invention include, for example, addition polymers (including addition polymers of perfluorovinyl compounds) or condensation polymers such as polyethers, poly(carboxylic acid derivatives) including polyesters, polyurethanes, epoxy resins, polysulfones, polycarbonates and polyamide-polyimides; preferably polycarbonates, polyesters, polyamides and polyimides, more preferably polyimides, liquid crystal polymers, especially polyesters, aromatic polyesters, aromatic polyamides and aromatic polycarbonates which are frequently intractable or have high melting points and poor melt flow characteristics above temperatures commonly used in shaping or molding polymers, when advanced to high molecular weights such as molecular weights greater than about 10,000. These materials are advantageously prepared from the oligomers or polymers by forming the trifluorovinyl group directly onto the terminal positions using chemistry such as taught in the preceding paragraphs or, more conveniently, by reacting

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a compound containing a trifluorovinyl group and a second functional group reactive with the terminal functionality of the oligomers or polymers. Examples of suitable second functional groups on the compound containing the trifluorovinyl group are carboxylic acid groups and their derivatives such as salts, acid halides, or esters; amines, either primary or secondary; hydroxyl; chloroformate or any number of other nucleophilic or electrophilic groups. Suitable terminal groups of the oligomers or polymers are the same as described for the trifluorovinyl containing compound. When one of the reactants has a given reactive group, the other has a functional group of opposite reactivity, for example nucleophilic with electrophilic. Preferably the perfluorovinyl group is incorporated as a perfluorovinyl ether, more preferably a perfluorovinyl aromatic ether, most preferably as the perfluorovinyl ether of an aromatic ester, as for example $\text{CF}_2=\text{CF}-\text{O}-\text{Ar}-\text{CO}-\text{O}-\text{oligomer}$ where Ar is an aromatic group. An example of the latter method of preparing the monomer and subsequently the polymer of the present embodiment of the present invention is the reaction of polycarbonate oligomer or other oligomer having terminal phenolic groups with 4-trifluorovinyloxybenzoyl chloride. The resulting oligomeric monomer is terminated with trifluorovinyl groups connected to the oligomer via ester groups formed in the reaction of the phenolic end groups with the acid chloride reactive site of the trifluorovinyl compound. The reaction is conveniently conducted by methods of forming esters from phenolics and acid chlorides. Oligomers, thus capped, are then thermally polymerized to a higher molecular weight polymer wherein the oligomer fragments are linearly linked by perfluorocyclobutane rings. Polymers, thus

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formed, retain substantial property similarity to high molecular weight resins of the oligomer structure. Preparation of trifluorovinyl compounds having second functional groups are prepared according to procedures outlined above and taught in copending U.S. Patent Application Serial Nos. 364,666, filed June, 1989, and 364,686, filed June 9, 1989. The 4-trifluorovinyloxybenzoyl chloride referred to above and related compounds are prepared from phenolic substituted aromatic esters by techniques taught in U.S. Patent 4,423,249, followed by hydrolysis to the acid and then conversion to the corresponding acid chloride. The above technique is equally applicable to polyfunctional compounds other than oligomers of polymers. Thus, a difunctional compound such as dihydroxybiphenyl can be reacted with the above acid chloride to form a bis(trifluorovinyl) monomer.

Another particularly useful embodiment of the present invention is the formation of linear, thermoplastic materials from monomers containing two trifluorovinyl groups. Generally monomers containing two vinyl groups result, by conventional addition polymerization, in highly crosslinked, brittle plastics. The present novel polymerization process is more akin to condensation polymerization in that difunctional monomers result in linear polymers. To obtain properties associated with structural plastics, it is preferred that R in Formula I is aromatic and most preferred that R contains more than one aromatic ring. It is also preferred that each X is oxygen or sulfur (optionally as sulfone or sulfoxide) and most preferably oxygen. The resulting aromatic perfluorocyclobutyl ether backbone in the thus formed polymers have

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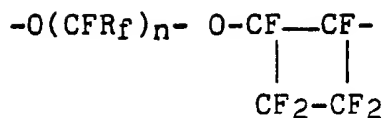
exceptional physical properties combined with excellent melt processability on conventional thermoplastic fabrication equipment. A polymer exemplary of these characteristics is represented by Formula II wherein R is biphenyl, m is 1, and each X is oxygen. The monomer is conveniently prepared from 4,4'-dihydroxybiphenyl and dibromotetrafluoroethane by modification of chemistry described in U.S. Patent No. 4,423,249 or by the process disclosed in copending U.S. Application Serial No. 364,665, filed June 9, 1989. The monomer is easily polymerized at a convenient rate by heating in bulk or solution at 150°C to 200°C. Typical properties of a polymer prepared in perfluorotetradecahydrophenanthrene solvent are a glass transition temperature of about 170°C, tensile strength (as measured by the procedure of ASTM D-882-83) of from 5,000 to 6,000 psi (pounds per square inch), percent elongation (as measured by the procedure of ASTM D-882-83) of from 10 percent to 20 percent, tensile modulus (as measured by the procedure of ASTM D-882-83) of from 200,000 to 300,000, dielectric constant (as measured by the procedure of ASTM D150-87) of from 2.25 to 2.65, and static dissipation factor (as measured by the procedure of ASTM D150-87) of from 0.0001 to 0.0008.

Another preferred embodiment of the present process is to form linear perfluoropolymers, preferably having ether atoms incorporated in the polymer backbone. Polymers of this general class of compounds are generally prepared by fluoride ion catalyzed reactions of perfluorinated epoxides described in U.S. Patent Nos. 3,214,478 and 3,322,826. These type products having perfluorocyclic groups, including perfluorocyclobutane groups, are taught in U.S. Patent No. 3,303,145. While

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the methods taught are suitable for preparing low molecular weight materials, the method is generally unsuitable for producing higher molecular weight products (for example, average molecular weights at least about 10,000). Elimination of fluoride to form acid fluoride terminal groups in the growing chains generally limits molecular weight. This deficiency can be offset somewhat by lowering reaction temperature, but nevertheless the only commercially significant products produced using a process like that taught in the prior art patents are oligomeric fluids such as Krytox™ commercially available from I. E. DuPont and Company. Formation by the cyclopolymerization process of the present invention makes possible production of higher molecular weight polymers. Preferable perfluoro polymers of this embodiment of the present invention are thermally produced from monomers of Formula I wherein R is perfluoroalkyl, X is oxygen. These monomers are conveniently produced by known chemistry involving reaction of perfluoroalkyl compounds having two acid fluoride groups with fluoropropyl epoxides followed by decarboxylation to form vinyl ethers as described in U.S. Patent Nos. 3,450,684 and 4,554,112. The resulting monomers, perfluoroalkyl diperfluorovinyl ethers, $\text{CF}_2=\text{CFO}(\text{CFR}_f)_n\text{OCF}=\text{CF}_2$, where R_f is branched or linear fluoroalkyl (preferably of from 1 to 10 carbon atoms), or fluorine; and n is preferably between 1 and 10, are then thermally polymerized to form polymers, or if desirable, oligomers having the repeating unit,

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and terminated in trifluorovinyl ether groups. The polymers having average molecular weight above about 10,000, preferably above about 25,000 are useful in elastomer applications, particularly when cured by a crosslinking reagent. Suitable crosslinking reagents are monomers described herein where m is greater than 1. The terminal groups are conveniently further reacted, if desired, by a variety of processes within the skill in the art including radical initiated reactions or, alternately, are rendered inert by halogenation, preferably with fluorine. It is within the scope of the present invention to copolymerize the foregoing monomers, oligomers or polymers with other compounds of the present invention having two or more trifluorovinyl groups. For instance, oligomers of the divinylperfluoroethers are formed and cured with a perfluorovinyl compound, particularly of Formula I wherein R is aromatic, m is 2 and both X's are oxygen. This technique is useful for forming thermoset resins or elastomers depending on the proportion of multifunctional (m greater than 1) material used.

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Polymers of the present invention are suitably solids, fluids or gels, preferably solids or fluids, most preferably solids. The solids preferably maintain plastic characteristics such as tensile strength well above ambient temperatures (for example, above about 25°C) and have glass transition temperatures from well

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below ambient to well above ambient temperatures. A particularly preferred group of such polymers have glass transition temperatures (T_g) above ambient (25°C), preferably above 60°C and most preferably above 100°C . In general, the polymers having T_g above ambient result from monomers of Formula I wherein R is aromatic, and the polymers having T_g above 60°C when R contains more than one aromatic ring. A particular desirable property of polymers where R is aromatic and not substituted with polar substituents (for example, nitro, sulfonate, carboxy) is the combination of good physical properties and good electrical properties. Dielectric constants and static dissipation factors (as measured according to the procedures of ASTM D150-87) preferably range from 2.2 to 3.0 and from 0.0001 to 0.005 respectively. Glass transition temperatures increase from about ambient when R is phenyl, to about 170°C when R is biphenyl, to about 230°C when R is 9,9-diphenylfluorene, to about 286°C or higher when R is 1,1,1-triphenylethane.

The linear polymers are advantageously thermoformed as by molding or extruding or are cast from solvents such as ethers and chlorinated solvents, for instance, tetrahydrofuran or dichloromethane. The polymers possess processing advantages over other polymers having similar low dielectric properties such as polytetrafluoroethylene. The advantages include extrudability, suitability for injection molding and solvent casting.

Before backbone crosslinking, substantially linear polymers or oligomers are thermally produced from the preferred monomers. The polymers can be crosslinked by any crosslinking initiating means such as by heat, by

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free radicals, or by wave energy. This crosslinking preferably occurs substantially without crosslinking agents such as monomers having three or more functional groups reactive to form the polymers (trifluorovinyl groups). By substantially without, it is meant that while materials which act as crosslinking agents or catalysts for crosslinking may incidentally be present in very small quantities, preferably less than about 0.01 weight percent of the polymer, more preferably less than about 0.01 weight percent crosslinking agent and less than about 0.001 weight percent catalyst for crosslinking, such materials are not deliberately added. Free radicals are suitably provided by use of any means of supplying free radicals such as by use of compounds known in the art for producing free radicals, for example, organic azo compounds. Wave energy is suitably supplied by means such as ultraviolet light, radiant heat (for example, infrared light), microwaves, X-rays, or particle beam radiation. Such means are within the skill in the art. Neither thermal crosslinking nor crosslinking using wave energy require addition of a catalyst such as a free radical initiator and such methods are, therefore, preferred. Thermal crosslinking is, however, more preferred.

Thermally backbone crosslinked polymers are prepared from such thermally formed polymers containing perfluorocyclobutane rings by heating the polymers to a temperature sufficient to result in crosslinking, that is for chemical bonds to form between at least some of the polymer molecules. The temperature for such crosslinking is higher than that required for thermal (linear) polymerization, preferably it is at least about 50°C degrees higher than the temperature required for

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5 thermal (linear) polymerization, more preferably from 250°C to 400°C, most preferably from 280°C to 380°C, even more preferably from 280°C to 340°C. These temperatures are suitably maintained for a time sufficient to achieve a preselected degree of crosslinking. Such times are preferably from 1 minute to 10 days, more preferably from 15 minutes to 1 day (24 hours), most preferably from 15 minutes to 8 hours.

10 A particularly useful aspect of the present invention includes preparing the substantially linear polymers according to processes previously taught and exposing the linear polymer to conditions suitable for backbone crosslinking in a shaping apparatus, for
15 example, an extruder, a mold, or other apparatus suitable for heating or other crosslinking initiation, for example, for a time and at a temperature sufficient for crosslinking. This allows handling of a polymer which melts at a relatively lower temperature and
20 producing an elastomer or thermosetting polymer having stability at temperatures sufficient to melt the substantially linear polymer. Crosslinking advantageously occurs without the need for a solvent or
25 a high pressure apparatus, and proceeds without the evolution of volatile compounds or by-products.

Crosslinked polymers formed by the process of the invention differ from crosslinked polymers prepared
30 from monomer mixtures containing monomers having more than two perfluorovinyl groups in that they are prepared directly from bifunctional monomers or thermoplastic polymers thereof without addition of a catalyst or a multifunctional crosslinking agent. Also, polymers prepared from a single monomer having more than one

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crosslinking agent in general have a very high crosslink density and are more rigid and inflexible solids than polymers crosslinked by the process of the present invention.

5 The following examples are offered to illustrate but not to limit the present invention. In each case, percentages are weight percent unless otherwise indicated. Examples (Ex.) of the present
10 invention are indicated numerically, while comparative samples (C.S.) are not examples of the present invention and are indicated with letters.

 All gas chromatography/mass spectrometry
15 (GC/MS) analyses of monomers and intermediates are performed on a Finnigan 1020 GC/MS using a 30 meter RSL-150 fused silica capillary column. All GC/MS analyses of fluid polymer samples are performed on a
20 Finnigan 4500 GC/MS using a 60 meter DB-1 fused silica capillary column, with the GC program run at 290°C isothermal. Mass to charge (M/e) ratios and percentage (%) of peak height relative to tallest (parent) peak are given. Liquid chromatography/mass spectrometry (LC/MS)
25 is performed on a Finnigan 4500 mass spectrometer using acetonitrile - water eluent and a moving belt LC/MS interface.

 Dynamic Mechanical Spectroscopy (DMS)
30 measurements are performed on a Rheometrics RDS-7700 rheometer in torsional rectangular geometry mode using 60mm x 12mm x 3mm samples at 0.05 percent strain and 1 Hertz (Hz). Differential scanning calorimetry (DSC), thermomechanical analysis (TMA) and thermogravimetric

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analysis (TGA) is performed on a Perkin Elmer 7000 thermal analysis system unless otherwise indicated.

5 Dielectric constant and dissipation factor measurements are conducted according to the procedures of ASTM D150-87. Tensile strength and modulus and percent elongation were measured on an Instron model 1125 according to the procedures of ASTM D-882-83.

10 Gel Permeation Chromatography (GPC) is performed on a Waters 720 GPC instrument using a methylene chloride eluent and a series of Micro-Styrigel™ columns of 10,000, 1,000, 500 and 100 angstrom pore sizes. Reported values are
15 standardized against polystyrene.

Granular zinc is activated by washing in 0.1 normal (N) hydrochloric acid (HCl) followed by drying in a vacuum oven at 0.5 mmHg (66.5 Pa) and 140°C
20 for 10 hours.

Infrared (IR) spectra are measured on a Beckmann Microlab 600 model spectrophotometer. Nuclear
25 Magnetic Resonance (NMR) spectra are measured on a Varian EM360 spectrometer using 19F (fluorine 19) or 1H (hydrogen) mode.

The gel point determination involves a dynamic
30 mechanical spectroscopy technique performed at 10 percent strain in a parallel plate mode using 1 mm gap. Storage and loss moduli are measured at frequencies from 0.1 to 100 radians per second, measuring 10 different frequencies per decade of frequency, every 15 minutes. Measurements are carried

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out isothermally. The ratio of the loss modulus (G'') to the storage modulus (G'), known as the loss tangent, or $\tan \delta$ (G''/G'), is plotted against time for a number of frequencies. The point at which the value of $\tan \delta$ becomes independent of frequency (as is indicated by a convergence of plots of the $\log \tan \delta$ versus time at various frequencies to a point) is known as the gel point, and represents the time at which the size of the polymer chains in the sample increase to a size which is on the order of the size of the sample. At this point the sample is considered crosslinked on a macromolecular scale, and exhibits properties such as enhanced mechanical strength and insolubility in solvents for the thermoplastic precursor.

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EXAMPLE 1: PREPARATION AND BULK POLYMERIZATION OF
4,4'-BIS(TRIFLUOROVINYLOXY)BIPHENYL

Dimethyl sulfoxide (DMSO) (1800 mL) was placed in a 5-liter 5-necked flask fitted with a mechanical stirrer, a Dean-Stark phase separating trap topped with a nitrogen padded reflux condenser, and a thermocouple attached to a temperature controller. The solvent was stirred and purged of oxygen by blowing in nitrogen through a dip-tube placed below the surface of the liquid while 4,4'-dihydroxybiphenyl (454g, 2.44 mole) was added to the flask.

30

The system was stirred and purged for 20 minutes, then potassium hydroxide (85 percent pellets) (322g, 4.88 mole) was added slowly. The stirred mixture was then heated to 120°C. The temperature was held at 120°C for 1.5 hours, then the heat was turned off and the mixture was allowed to cool

to room temperature. Toluene (600 mL) which had been thoroughly purged with nitrogen was added to the solution and the resulting mixture was heated to reflux (135°C). Water was azeotropically removed from the reactor through the Dean-Stark trap for a total of 5 4 days, cooling the reactor once after 24 hours to allow for salt formation to be broken up by opening the flask under a nitrogen sweep and scraping the sides with a spatula. After 4 days the Dean-Stark trap was removed 10 and replaced with a Soxhlet extractor containing anhydrous sodium sulfate. The toluene was then refluxed through the Soxhlet extractor for 7 hours to dry the toluene. After 7 hours, the Soxhlet was replaced with a Dean-Stark trap, and toluene (300 mL) was removed from 15 the reactor by simple distillation. The reaction mixture was then cooled to 30°C in an ice water bath and 1,2-dibromo-tetrafluoroethane (1300 g, 5.00 mole) was added slowly dropwise over three hours at a rate that maintained a reactor temperature of 35°±2°C. When the 20 addition was complete the reaction temperature was allowed to stabilize (not increasing in temperature when the ice bath was removed) and then a heating mantle was applied to the flask. The reactor was heated to 50°C 25 for 8 hours, then allowed to cool to room temperature with constant stirring. The crude reaction mixture was filtered to remove the potassium bromide salts, and the precipitate is washed with acetone. The filtrates were combined and thoroughly evaporated to remove acetone, 30 DMSO and residual toluene. The solid residue was subjected to a 2-liter Kugelrohr bulb-to-bulb distillation to provide the crude product. This

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material was dissolved in 750 mL of methylene chloride and was washed first with mild aqueous potassium bicarbonate (500 mL, approximately 0.2 M), then with mild aqueous hydrochloric acid (HCl) (500 mL, approximately 0.05 M), then twice with distilled water (500 mL each). After complete phase separation the product layer was removed and evaporated, and the residue was fractionally distilled (138°C to 148°C, 0.35 mmHg (46.5 Pa)) to provide 1031.1 g (1.90 mole, 77.9 percent yield) of 4,4'-bis(2-bromotetrafluoroethoxy)biphenyl, melting point 71°C to 73°C. The Infrared (IR) spectra of the product has the following peaks (cm⁻¹): 1601, 1492 (indicating an aromatic double bond); 1199-1107 (indicating carbon-oxygen and carbon fluorine bonds); 842, 788 (indicating aromatic character). The gas chromatograph/mass spectrometer (GC/MS) indicated peaks at the following mass to charge ratios (m/e) = 545 (29.8%); 543 (48.9%); 541 (23.8%); 365 (48.7%); 363 (50.9%); 337 (30.3%); 335 (34.7%); 168 (33.7%); 156 (78.3%); 140 (36.7%); 139 (90.1%); 129 (37.4%); 128 (100.0%); 127 (33.2%); 102 (32.9%); 76 (41.1%); 63 (34.3%), consistent with a product of 4,4'-bis(2-bromotetrafluoroethoxy)biphenyl.

25

Bromine was eliminated from this product by the following procedure:

Into a 1-liter 5-necked flask equipped with a mechanical stirrer, a thermocouple attached to a temperature controller, a powder addition funnel and a reflux condenser, was placed freshly distilled diglyme (200 mL) and fresh zinc powder (36.0g, 0.55 mole).

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The mixture was stirred and heated to 130°C. Powdered 4,4'-bis(2-bromotetrafluoroethoxy)biphenyl (100g, 0.184 mole) was added very slowly via the powder addition funnel over 3.5 hours. The mixture was then stirred mechanically at 115°C for 1 hour, after which heating was turned off and the mixture was allowed to cool to room temperature. The solution was centrifuged to remove the zinc salts. Then the liquid was decanted, and the zinc salts were washed with acetone and centrifuged again. The liquid portions were combined and evaporated thoroughly, and the residue was dissolved in methylene chloride and washed with 0.05 M hydrochloric acid. The methylene chloride solution was evaporated to provide 62.45 g (0.180 mole) of 4,4'-bis(trifluorovinyl)oxy)biphenyl of 94.5 percent purity in 98 percent yield.

The product was then recrystallized in an ethanol/water mixture to give product of 99.8 percent purity in greater than 70 percent recovery, melting point 44°C to 46°C.

The IR spectrum showed peaks at (cm⁻¹):
1833 (indicative of a perfluorovinyl group);
1601, 1491 (indicative of an aromatic double bond);
1231, 1196-1132 (indicative of carbon-oxygen and carbon-fluorine bonds respectively); 818 (indicative of aromaticity).

The GC/MS spectrum had the following peaks:
m/e: 346 (31.3%); 153 (13.8%); 152 (100.0%);
151 (27.0%); 150 (11.7%); 76 (14.9%); 63 (14.9%).

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Differential scanning calorimetry (DSC) analysis of the 4,4'-bis(trifluorovinyloxy)biphenyl monomer (20°C to 360°C at 20°C/minute) indicated a sharp endotherm of melting beginning at 45°C, followed by a broad exotherm beginning at about 170°C, interpreted as
5 corresponding to the heat of cyclization of the trifluorovinyl groups to form hexafluorocyclobutane rings.

10 The monomer, 4,4'-bis(trifluorovinyloxy)biphenyl, (15.0g, 0.043 mole) was placed in a nitrogen purged 100 mL round bottom flask and polymerized by heating at 210°C for 2 hours without stirring. After cooling, a small sample was removed for analysis by
15 differential scanning calorimetry (DSC). The sample shows a small crystalline melt with a peak at 60°C, followed by a broad exotherm beginning at about 200°C. The bulk sample was heated again at 235°C for an additional 3 hours. Again a sample was removed and
20 analyzed by DSC. The analysis indicated a very small crystalline melt with a peak at 60°C, followed by a low intensity exotherm beginning at about 230°C. The bulk sample was heated again to 265°C for 45 minutes.
25 Analysis of this sample indicated no crystalline melt and no exothermic activity up to and including 325°C, with the emergence of an endothermic glass transition (T_g) at 143°C.

30 **EXAMPLE 2: POLYMERIZATION OF 4,4'-BIS(TRIFLUOROVINYLOXY)BIPHENYL IN SOLUTION**

The monomer, 4,4'-bis(trifluorovinyloxy)biphenyl, (60.0g, 0.173 mole) was placed in a 1-liter 3-necked round bottom flask with 75 mL of

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perfluorotetra-decahydrophenanthrene (Multifluor™ APF 215 commercially available from Air Products). The flask was fitted with a mechanical stirrer and a nitrogen padded reflux condenser. After purging the flask thoroughly with nitrogen, the mixture was stirred and heated to reflux. Initially, upon heating the melted monomer was not miscible with the solvent, but as the temperature rose the two phases became homogeneous. After stirring at reflux for approximately 45 minutes, a polymer phase separated; and, after stirring at reflux for a total of 3 hours, the phase separated polymer became viscous enough to seize the stirring shaft. The cooled polymer was removed from the flask and evaporated under high vacuum (approximately 0.50 mmHg (66.5 Pa)) at about 220°C for 3 hours to remove residual solvent. A portion of this polymer was compression molded at 250°C to provide a light yellow, transparent flexible plastic film. Another portion was dissolved in tetrahydrofuran and placed in an evaporating dish to make a solvent-cast film. After the solvent was evaporated overnight, a light yellow thin film is peeled from the dish. This sample exhibited excellent flexibility and transparency.

An IR spectrograph of the film had the following peaks (cm⁻¹): 1601, 1490 (indicating aromatic double bonds); 1302, 1194-1115 (indicating carbon-oxygen and carbon-fluorine bonds), 818 (indicating aromaticity).

DSC analysis of this polymer indicated a T_g transition at 148°C.

Dynamic mechanical analysis (DMS) gave a T_g value of 170°C, and gel permeation chromatography (GPC)

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indicated a weight average molecular weight of 85,000 as standardized against polystyrene.

Dielectric constant and dissipation factor measurements performed on this polymer gave the following results:

	<u>Frequency (kHz)</u>	<u>Dielectric Constant</u>	<u>Dissipation Factor</u>
10	1.0	2.58	0.0007
	10.0	2.57	0.0004
	1000.0	2.55	0.0004

Examples 1 and 2 illustrate two types of polymerization of 4,4'-bis(trifluorovinyloxy)biphenyl. It is notable that the properties of each are roughly similar, with slightly more discoloration taking place in the bulk polymerization (according to the procedures of Example 1).

EXAMPLE 3: PREPARATION AND POLYMERIZATION OF 9,9-BIS(4'-[TRIFLUOROVINYLOXY]PHENYL)FLUORENE

Into a 2 liter 5-necked round bottom flask fitted with a mechanical stirrer, Dean-Stark trap topped with a nitrogen padded reflux condenser and a thermocouple attached to a temperature controller, were placed DMSO (650 mL) and toluene (200 mL). While the stirred solution is purged with nitrogen, 9,9-bis(4'-hydroxyphenyl)fluorene (200.0 g, 0.57 mole) was added to the flask. While purging with nitrogen continued, potassium hydroxide (85 percent pellets, 77.5 g, 1.17 mole) was added all at once, and the mixture was

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heated to 100°C with constant stirring. After two hours, the temperature was increased until the solution began to reflux (130°C). Water was removed by azeotropic distillation for 24 hours. The Dean-Stark trap was replaced by a Soxhlet extractor containing anhydrous sodium sulfate, and the toluene was refluxed through the Soxhlet for 5 hours. A small amount of toluene (60 mL) was then removed by simple distillation. Then the reactor was cooled to 35°C. Addition of 1,2-dibromotetrafluoroethane (315 g, 1.21 mole) via dropping addition funnel was then maintained at a rate that keeps the reaction temperature at 35°C to 38°C. When the addition was complete, the mixture was heated at 50°C for 8 hours, then cooled to room temperature with constant stirring. The mixture was filtered, and the precipitate was washed twice with acetone. The filtrates are combined and evaporated thoroughly. The residue from the evaporation was washed with water to remove residual potassium bromide (KBr). After the residue was air dried for 24 hours, it was extracted with hexane in a Soxhlet extractor. Evaporation of the hexane, followed by column chromatography of the residue (on neutral alumina, using hexane eluent) provided a product, 9,9-bis(4'-[2"-bromotetrafluoroethoxy]phenyl)-fluorene (331.4 g, 0.468 mole, 82 percent yield), melting point 157°C to 158°C.

The LC/MS spectrum had peaks at: m/e:

710 (53.0%); 709 (34.0%); 708 (100.0%); 707 (23.3%); 706 (49.8%); 513 (28.4%); 511 (28.5%); 438 (12.8%); 437 (52.4%); 436 (14.7%); 435 (55.8%); 355 (15.7%); 290 (33.9%); 289 (19.5%); 239 (35.9%); 228 (36.2%);

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227 (38.9%); 226 (47.3%); 202 (27.7%); 157 (47.2%);
131 (27.6%); 129 (23.1%).

5 The product from the above reaction (18.85g, 0.027 mole) was combined with freshly activated granular zinc (5.00g, 0.076 mole) in glyme and heated at reflux overnight. After cooling, the reaction mixture was decanted and centrifuged to remove suspended zinc salts. The solvent was removed by vacuum evaporation, and the
10 residue was purified by column chromatography on neutral alumina using hexane as an eluent to provide as product 9,9-bis(4'-trifluorovinyloxyphenyl)fluorene (5.55g, 0.011 mole, 40 percent yield), melting point 115°C to 116°C.

15

The LC/MS spectrum had peaks at: m/e:
511 (29.3%); 510 (91.9%); 337 (37.2%); 316 (16.1%);
315 (19.7%); 313 (12.8%); 241 (15.5%); 240 (52.8%);
239 (100.0%); 237 (15.6%); 207 (14.1%); 158 (28.7%);
20 157 (53.1%); 155 (14.4%); 150 (28.8%); 145 (18.3%);
144 (16.5%); 120 (15.1%).

25

Into a 50 mL round bottom flask fitted with a nitrogen padded reflux condenser, mechanical stirrer and a thermocouple attached to a temperature controller were placed 9,9-bis(4'-trifluorovinyloxyphenyl)fluorene (3.0g, 0.0059 mole) and diphenyloxide (5.0 mL). The mixture was stirred and heated to reflux (255°C) for
30 22 hours. The diphenyloxide (DPO) solvent was evaporated under high vacuum on a 100 milliliter Kugelrohr bulb to bulb apparatus (0.03 mm, 165°C) to provide the polymer product, which was dissolved in methylene chloride and cast into a thin film.

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Gel permeation chromatography analysis of the polymer indicated a weight average molecular weight of 135,000 as standardized against polystyrene.

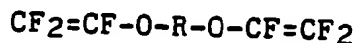
5 DSC analysis indicated a Tg transition at 224°C.

Example 3 illustrates preparation and polymerization of 9,9-bis(4,4'-trifluorovinyl-oxyphenyl)fluorene. It is notable that the resulting
10 polymer, which is polymerized in DPO, attains a high molecular weight and forms a solvent cast film with good physical properties such as flexibility. The polymer is soluble in acetone, dichloromethane and tetrahydrofuran.

15 EXAMPLES 4-9: PREPARATION AND POLYMERIZATION OF A VARIETY OF PERFLUOROCYCLOBUTANE RING-CONTAINING POLYMERS

The procedure outlined in Example 3 was
20 repeated for each of the indicated starting materials, except for the changes indicated in Table I and adjustments in amounts to maintain the stoichiometry of Example 3, to produce the indicated monomers of the structure:

25



wherein R is given in Table I

30

Table I: Preparation of Monomers

EX. NO.	Starting Material	R	Changes in Procedure
4	Resorcinol	1,3-Phenylene	Tetraglyme was used in second step. Product was distilled directly from reaction mixture under vacuum. *3-(1',1',2',2'-tetrafluoroethoxy)-trifluorovinylbenzene and 1,3-bisphenol(1',1',2',2'-tetrafluoroethoxy)trifluorovinylbenzene were isolated as by products and identified by GC/MS spectra consistent with those compounds.
5	4,4'-dihydroxy-biphenyl	4,4'-Biphenyl	See Example 1
6	4,4'-thiodiphenol	4,4'-Thiodiphenyl	Tetraglyme was used in second step, removed by diluting with methylene chloride and washing with water.
7	Bisphenol A	Isopropyl-2,2-diphenylene	
8	Hexafluorobisphenol A (bisphenol AF)	Hexafluoroisopropyl-2,2-diphenylene	
9	9,9-bis(4'-hydroxyphenyl)fluorene	9,9-bis(4'-phenylene)fluorene	See Example 3

The data in Table I shows that a variety of perfluorovinyl monomers are prepared by processes within the scope of the present invention.

5 The procedure outlined in Example 2 was repeated for each of the monomers in Table I, except for the changes in procedure indicated in Table II to produce polymers from the indicated monomers. The properties of these polymers are given in Table II.

10

Table II: Properties of Thermoplastic Polymers

Ex. No.	R	Tg (°C)	Dielectric Constant 10 kHz	Dissipation Factor 10 kHz	Weight Average Molecular Weight
4	1,3-Phenylene	32	2.41	--	41,400
5	4,4'-Biphenyl	170	2.57	0.0004	85,000
6	4,4'-Thiodiphenyl	78	2.62	0.0005	42,500
7	Isopropyl-2,2-diphenylene	98	--	--	50,700
8	Hexafluoroisopropyl-2,2-diphenylene	125	--	--	23,500
9	9,9-bis(4'-phenylene)fluorene (prepared in diphenyloxide)	224	--	--	135,000

30 The data in Table II shows that a variety of perfluorocyclobutane ring-containing polymers are prepared by processes within the scope of the present invention.

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EXAMPLE 10: PREPARATION OF 1,1,1-TRIS(4'-
-TRIFLUOROVINYLOXYPHENYL)ETHANE AND BULK POLYMERIZATION
THEREOF WITH 4,4'-BIS(TRIFLUOROVINYLOXY) BIPHENYL

5 A 1 liter 5-necked round bottom flask was
fitted with a mechanical stirrer, a Dean Stark trap
topped with a nitrogen padded reflux condenser, and a
thermocouple attached to a temperature controller. A
mixture of DMSO (450 mL), toluene (150 mL), and 1,1,1-
10 -tris(4'-hydroxyphenyl)ethane (55.1 g, 0.18 mole) was
added to the flask under nitrogen purge. After stirring
for 15 minutes under a vigorous nitrogen purge,
potassium hydroxide (85 percent pellets, 80.0g,
1.2 mole) was slowly added to the reaction flask. The
15 mixture was then stirred at reflux for 48 hours with
azeotropic removal of water. The resulting suspension
was cooled to 35°C in an ice bath and 1,2-
dibromotetrafluoroethane (155 g, 0.60 mole) was added at
20 a rate that maintained a temperature of 30°C to 35°C.
When the addition was complete, the mixture was heated
to 50°C with continuous stirring for 3 hours. After
filtration, the solvents were removed by heating under
vacuum on a rotary evaporator. The brown residue was
25 purified by column chromatography on neutral alumina
using hexane as eluent to provide as product
1,1,1-tris(4'-[2"-bromotetrafluoroethoxy]phenyl)ethane
(18.3 g, 0.022 mole, 12 percent yield).

30 Identity of the product was confirmed by a
GC/MS spectrum, the following peaks: m/e: parent ions
m/e 840-842-844-846 (ratio 1:3:3:1) too heavy to detect.
Structure determined from fragmentation: 573 (32.3%);
571 (58.3%); 569 (31.5%) [indicating parent
-PhOCF₂CF₂Br]. 299 (58.1%); 297 (52.7%); 279 (32.3%);

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228 (43.5%); 227 (31.5%); 226 (36.0%); 215 (59.5%);
181 (82.1%); 179 (100.0%); 165 (50.3%); 152 (43.7%);
131 (47.1%); 129 (50.4%); 100 (38.8%).

5 Into a 500 mL 5-necked flask fitted with a
mechanical stirrer, a reflux condenser, and a
thermocouple attached to a temperature controller was
placed freshly activated granular zinc (4.3 g,
0.066 mole) and 25 mL dry diglyme. This mixture was
10 stirred and heated to 110°C under nitrogen while the
product from the above reaction (18.0 g, 0.021 mole) was
dissolved in 21 mL diglyme and added dropwise. The
resulting mixture was stirred at 115°C for 3 hours, then
cooled and filtered. The filtrate was evaporated at
15 60°C under vacuum to remove the diglyme, and the residue
was purified by column chromatography on neutral alumina
using hexane as eluent to provide the product 1,1,1-
-tris(4'-trifluorovinyloxyphenyl)ethane (9.98 g,
0.018 mole, 8 percent yield).

20 The GC/MS spectrum had the following peaks:
m/e: 546 (3.2%); 531 (44.0%); 434 (17.9%); 373 (24.4%);
276 (16.9%); 240 (28.1%); 239 (73.9%); 199 (19.3%);
25 178 (100.0%); 177 (17.8%); 176 (25.4%); 163 (17.3%);
152 (31.9%); 151 (17.8%); 127 (20.3%); 126 (28.7%);
120 (39.1%); 119 (70.3%); 118 (25.6%); 113 (27.3%);
107 (18.8%); 102 (31.7%); 77 (15.9%); 76 (29.5%).

30 This example illustrates preparation of a
trifunctional monomer, 1,1,1-tris(4'-trifluorovinyl-
oxyphenyl)ethane. This monomer is useful alone or mixed
with a bifunctional monomer to produce a crosslinked
perfluorocyclobutane polymer.

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A mixture of 4,4'-bis(trifluorovinyloxy)-biphenyl (as prepared in Example 1) (4.50 g, 0.013 mole) and the 1,1,1-tris(4'-trifluorovinyloxyphenyl)ethane (0.79 g, 0.0014 mole) were combined in a 100 mL single-necked round bottomed flask topped with a nitrogen padded reflux condenser. The flask was purged thoroughly with nitrogen, and the mixture was heated without stirring. After reaching a temperature of 200°C, the mixture set into a rigid plastic within 15 minutes. This material was then cured an additional 40 minutes at 220°C; then the heat was removed. The resulting plastic was rigid, inflexible and did not dissolve in tetrahydrofuran (THF) or methylene chloride, but swelled into a gel in these solvents.

DSC analysis (25°C to 350°C, 20°C/minute) of this polymer sample showed a slight endothermic event at 125°C followed by a broad exotherm beginning at about 210°C, indicative of an incompletely cured polymer. After this sample was cured during the first DSC scan, a second scan was run which clearly indicates a Tg transition at 151°C and no subsequent exothermic activity at higher temperatures.

Example 10 illustrates preparation of 1,1,1-tris(4'-trifluorovinyloxyphenyl)ethane and copolymerization thereof 4,4'-bis(trifluorovinyloxy)-biphenyl therewith. The resulting polymer was stiff and brittle, as well as insoluble, compared to the thermoplastic of Example 2, prepared from 4,4'-bis(trifluorovinyloxy)biphenyl alone, which was flexible and soluble in THF and methylene chloride.

EXAMPLE 11: BULK POLYMERIZATION OF 4,4'-
-BIS(TRIFLUOROVINYLOXY)BIPHENYL WITH SUBSEQUENT ADDITION
OF 1,1,1-TRIS(4'-TRIFLUOROVINYLOXYPHENYL)ETHANE

5 Monomer 4,4'-bis(trifluorovinyloxy)biphenyl
 (16.2 g, 0.047 mole) was placed in a 500 mL round bottom
 flask along with a magnetic stirring bar. A nitrogen
 padded reflux condenser was placed on the flask, and the
 monomer was heated at 200° to 205°C with stirring for
10 20 minutes, to form a low molecular weight polymer
 resembling a thick fluid at 200°C. The fluid was
 allowed to cool to room temperature where it sets into a
 brittle glass. The glass was dissolved in methylene
 chloride and 1,1,1-tris(4'-trifluorovinyloxyphenyl)-
15 ethane (0.51 g, 0.00094 mole) was added to the solution.
 The methylene chloride was evaporated and the residue
 was dried and devolatilized on a Kugelrohr bulb to bulb
 apparatus at 120°C to 140°C and 0.20 mmHg (26.6 Pa)
20 pressure. While still hot, the fluid mixture was poured
 into a mold and cured on a hot press at 250°C and
 20,000 psi for one hour. The mold was removed from the
 press and cooled. A coupon was removed from the mold.
 The coupon was a strong and flexible plastic, and did
25 not dissolve in THF but swelled into a gel therein.

 DSC analysis of this crosslinked polymer sample
 indicated a Tg value of 149°C, with no subsequent
 thermal activity up to and including 350°C.
30

 Example 11 illustrates polymerization of
 4,4'-bis(trifluorovinyloxy)biphenyl with subsequent
 addition of 1,1,1-tris(4'-trifluorovinyloxyphenyl)-
 ethane. It is notable that crosslinked polymers are
 prepared either by copolymerizing difunctional and

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multi-functional monomers, as in Example 10, or by combining a multifunctional monomer with a low molecular weight polymer containing trifluorovinyl end groups as in Example 11.

5 EXAMPLE 12: PREPARATION OF 1,4-BIS(TRIFLUOROVINYL)BENZENE AND BULK POLYMERIZATION THEREOF

10 A 5 liter 3-necked round bottom flask was fitted with a mechanical stirrer, a nitrogen padded reflux condenser and a rubber septum. Glyme (100 mL) and activated zinc granules (11.50 g, 0.18 mole) were added to the flask along with a magnetic stirring bar.

15 The flask was then purged with nitrogen for 15 minutes, after which time iodotrifluoroethylene (20.3 g, 0.098 mole) was added slowly via syringe through the septum. After 20 minutes of stirring the mixture began to turn brown and get warm. After 2 hours a white

20 precipitate began to form. After stirring was continued without heat for 4 hours, the flask was opened under a slow nitrogen purge and 1,4-diiodobenzene (16.0 g, 0.0485 mole) was added along with palladium tetrakis-

25 (triphenylphosphine) (0.57 g, 0.00049 mole). The mixture was stirred overnight, resulting in the formation of a large amount of suspended solid. The reaction was allowed to stir an additional 24 hours, after which it was filtered, and the precipitate was

30 washed with hexane (3 times with 50 mL each wash). The filtrates were combined and evaporated at 30°C on a rotary evaporator to provide a residue which was purified by column chromatography (neutral alumina, hexane eluent) to give 7.50 g of $\text{CF}_2=\text{CF}-\text{Ph}-\text{CF}=\text{CF}_2$ as product (0.0315 mole, 65 percent yield). This product

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was analyzed by GC/MS and gave the following spectrum:
m/e: 238 (100 percent); 188 (12.0%); 187 (46.4%);
169 (92.0%); 138 (18.8%); 99 (16.3%); 81 (12.3%);
69 (30.1%). The material is found to be air sensitive,
fuming acid gasses if left exposed to oxygen.

5

This example illustrates preparation of an
aromatic monomer having two perfluorovinyl groups
directly attached to the aromatic ring and illustrate
the use of iodotrifluoroethylene in preparation of a
monomer. This preparation proceeds via a one pot
synthesis to give good yields of the monomer.

It was noted that when a sample of this
material was stored for 10 hours or more in contact with
air that a highly mobile gel was formed along with the
evolution of acid fumes. This observation was believed
to be indicative of formation of acyl fluorides and
fluoride ions, and of addition polymerization (rather
than cyclization) catalyzed by the fluoride ion. The
result of such storage in contact with air differs from
the following product in that only a very low molecular
weight gel was formed, with a high degree of
crosslinking taking place in the gel matrix.

Monomer 1,4-bis(trifluorovinyl)benzene
(1.00g, 0.0042 mole) was placed in a 100 mL round bottom
flask with a magnetic stir bar and purged with nitrogen.
The neat monomer was heated to about 80°C with slow
stirring. In 10 minutes the monomer set into a hard
glassy polymer which was not soluble in THF or methylene
chloride, but which turned brown and fumes acid gasses
when left exposed to air overnight. This observation
suggested that a low molecular weight polymer was formed

30

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and contained unreacted trifluorovinyl groups which were still air sensitive.

5 Example 12 illustrates polymerization of an aromatic monomer having two perfluorovinyl groups directly attached to the aromatic ring, which polymerization proceeds in a very short time and without the need of solvents.

10 EXAMPLE 13: SOLUTION POLYMERIZATION OF 1,4-BIS(TRIFLUOROVINYL)BENZENE

 Monomer 1,4-bis(trifluorovinyl)benzene (1.00 g, 0.0042 mole) was combined in a 100 mL round bottom flask with 2.0 g of perfluorotetradecahydrophenanthrene (Multifluor™ APF-215 commercially available from Air Products) and a magnetic stirrer. The flask was topped with a nitrogen padded reflux condenser. When the mixture was purged with nitrogen, it was heated to reflux with stirring. After 10 minutes, a crystalline precipitate was formed. This precipitate was isolated by filtration followed by vacuum drying.

25 The material was insoluble in THF or methylene chloride. A powder was formed by crushing the polymer precipitate in a mortar and pestle. Analysis of the powder by DSC indicates two small exothermic events, one at 180°C to 240°C, the other at 320°C to 380°C leading into decomposition.

 Example 13 illustrates solution polymerization of an aromatic monomer having two perfluorovinyl groups directly attached to the aromatic ring. This polymerization proceeds very quickly at higher

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temperatures and in the presence of inert solvents such as that used above.

EXAMPLE 14: PREPARATION AND POLYMERIZATION OF
4,4'-BIS(TRIFLUOROVINYL)BIPHENYL

5

A 1 liter 5-necked round bottom flask was fitted with a mechanical stirrer, a nitrogen padded reflux condenser and a rubber septum. Dry glyme (300 mL) and activated zinc granules (50.8 g, 0.395 mole) were added to the flask as it was purged thoroughly with nitrogen. Then iodotrifluoroethylene (100.0g, 0.48 mole) was added to the flask all at once, and the mixture was stirred continuously under nitrogen for 5 hours. 4,4'-Diiodobiphenyl (97.0 g, 0.24 mole) was added to the flask along with nitrogen purged dimethylformamide (DMF) (300 mL) and palladium tetrakis(triphenylphosphine) (4.35 g, 0.0038 mole). The mixture was stirred at room temperature.

20

After 24 hours, a GC/MS of the mixture allowed identification of all the reaction components. After 72 hours, the reaction seemed to stop proceeding while excess diiodobiphenyl remained; another batch of iodotrifluoroethylene (25.0 g, 0.12 mole) was reacted with zinc in THF and added to the reaction mixture along with 1.0 g of palladium tetrakis(triphenylphosphine) catalyst. The reaction was allowed to stir an additional 12 hours, then was removed and evaporated to dryness under high vacuum on a rotary evaporator. Residue from evaporation was added to a 3 fold volumetric excess of water. A heavy precipitate was formed which was filtered and air dried on a vacuum funnel. The precipitate was dissolved in THF and

25

30

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5 filtered. Resulting filtrate was coated on silica gel by adding the silica gel to the THF solution and evaporating to dryness. This silica gel was then eluted on a short silica gel column using hexane as eluent to remove the colored material from the product. A fine
10 white crystalline material remained after evaporation of the hexane. This crystalline material was then chromatographed again carefully on an alumina column using hexane as an eluent. The first band to elute from the column was the desired monomer product $\text{CF}_2=\text{CF}-\text{Ph}-\text{Ph}-\text{CF}=\text{CF}_2$. A total of 44.2 g of product was recovered (58.7 percent yield).

15 The crystalline product has a melting point of 83°C to 84.5°C.

20 Analysis by GC/MS gave the following mass spectral data for this product: m/e: 314 (100.0%); 263 (13.4%); 243 (14.9%); 69 (13.0%).

25 DSC analysis of this monomer showed a sharp endotherm at about 82°C followed closely by a broad exotherm corresponding to cyclization of the trifluorovinyl groups beginning at about 98°C. A second exothermic event began at about 300°C leading into decomposition at greater than 400°C. The monomer was also oxidatively unstable, as indicated by turning brown and releasing acid fumes when allowed to stand in air.

30

Example 14 illustrates preparation of another aromatic monomer having two perfluorovinyl groups directly attached to the aromatic ring. Because of the crystalline nature of this product, a gel is not formed on standing, although oxidative decomposition does

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appear to evolve acid gasses at a somewhat slower rate than the product of Example 12.

5 A sample of the 4,4'-bis(trifluorovinyl)bi-phenyl (1.6 g, 0.005 mole) and fresh anhydrous DMF (5.0 mL) were added to a 100 mL single necked round bottom flask with a thermometer port along with a magnetic stirrer. The flask was topped with a nitrogen padded reflux condenser and stirring was begun as
10 nitrogen was allowed to pass out of the thermometer port. After 5 minutes of nitrogen purge, a thermocouple was placed in the thermometer port and heating was begun. The solution was heated to 40°C for 4 hours with no apparent reaction. The temperature was then raised
15 in 10°C increments, holding each new temperature for at least 45 minutes before proceeding to the next higher temperature. After the mixture was stirred at 130°C for 2 hours with no apparent change, the temperature was raised to 135°C and left to stir overnight. The next
20 morning the mixture was somewhat darker and noticeably higher in viscosity. The temperature was then raised to 140°C for 9 hours, after which the mixture becomes very thick, at which time heating and stirring were stopped.
25 A sample of the viscous liquid was removed and evaporated to dryness under vacuum, leaving a brittle crystalline powder. This powder dissolved in methylene chloride but did not filter through a 5 micron filter. Only a few drops of filtrate were recovered, and this
30 filtrate was analyzed by gel permeation chromatography as standardized against polystyrene. As recovered by this method, the soluble portion of the polymer had a weight average molecular weight of 41,600.

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DSC analysis of the crystalline polymer showed no thermal activity up to and including 400°C, with apparent decomposition beginning at about 420°C. All of the polymer samples prepared from this monomer were still air sensitive, as was evidenced by fuming of acid gasses after standing in air.

Example 14 illustrates polymerization of an aromatic monomer having two perfluorovinyl groups directly attached to the aromatic ring. This example also illustrates that careful temperature control may be employed to control the rate and extent of polymerization.

EXAMPLE 15: PREPARATION OF A FLUID POLYMER OF 1,3-BIS(TRIFLUOROVINYLOXY)BENZENE AND 3-TRIFLUOROVINYLOXY-1',1',1'-TRIFLUOROTOLUENE

To synthesize m-trifluorovinyloxy-1',1',1'-trifluorotoluene, DMSO (400 mL), toluene (140 mL), and 3-trifluoromethylphenol (81.0 g, 0.50 mole) were placed in a 1 liter 3-necked flask equipped with a mechanical stirrer, a Dean-Stark trap and a thermocouple attached to a temperature controller. The stirred solution was purged of oxygen by placing a dip tube below the surface of the solution and allowing nitrogen to be blown into the solution for 15 minutes. Potassium hydroxide (85 percent pellets, 33.7g, 0.51 mole) was added to the flask all at once, and a line to supply nitrogen was attached to a reflux condenser which was placed on top of the Dean-Stark trap. The mixture was then heated to 145°C and water was removed azeotropically. When water ceased to collect in the Dean-Stark trap, the temperature of the reaction was increased to 155°C and

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100 mL of toluene was removed by distillation, leaving a reaction mixture in the flask.

The reaction mixture was cooled to room temperature, and 1,2-dibromotetrafluoroethane (132.0 g, 0.51 mole) was added slowly using a dropping addition funnel. The mixture was heated to 55°C for 5 hours, then allowed to cool to room temperature. After the suspended solids have settled, the liquid was decanted away from the precipitate and was retained as a mixture of product in DMSO, which was added to a 3 times volumetric excess of water in a separatory funnel and shaken vigorously. The product formed a separate, lower layer at the bottom of the funnel and was removed. This crude product (lower layer) was washed again with 500 mL of water. After drying the washed lower layer over anhydrous magnesium sulfate, the crude product was fractionally distilled. The product, m-(2-bromo-tetrafluoroethoxy)-1',1',1'-trifluorotoluene (169°C to 171°C, 150 mmHg (19950 Pa)) gave the following mass spectral data: m/e: 342 (20.1%); 340 (19.8%); 323 (7.9 %); 321 (7.2 %); 211 (25.6 %); 145 (100.0%).

The product of the above reaction (56.0g, 0.164 mole) was combined with granular zinc (12.0g, 0.18 mole) in dry tetraglyme and stirred at 115°C for 6 hours to form a reaction mixture. The mixture was cooled to room temperature, and a distillation head was placed on the reaction flask. The product was then distilled directly out of the crude reaction mixture (108°C to 110°C, 150 mmHg (19950 Pa)) to give 40.5 g of the product, m-trifluorovinyloxy-1',1',1'-trifluorotoluene, which was 78 percent pure by GC analysis, with the remainder of the product being the

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by-product m-(1,1,2,2,-tetrafluoroethoxy)-1',1',1'-trifluorotoluene.

The product gave the following mass spectral data: m/e: 242 (52.3%); 223 (12.3%); 195 (14.2%);
5 145 (100%); 125 (18.3%); 95 (30.6%).

A mixture was prepared from 1.25 mL of 1,3-bis(trifluorovinyl)benzene (as prepared in Example 4) and 8.75 mL of 3-trifluorovinyl-1',1',1'-
10 -trifluorotoluene to make a total of 10 mL. This mixture was placed in a 50 mL round bottom flask fitted with a nitrogen padded reflux condenser and was refluxed under nitrogen for 20 hours.

15 The resulting product was analyzed by GC/MS and found to be a mixture of hexafluorocyclobutane products whose major components were 1,2-bis(3'-trifluoromethylphenoxy) hexafluorocyclobutane and 1,3-bis(2'-[3"-
20 -trifluoromethylphenoxy]hexafluorocyclobutyl)phenyl ether (having two perfluorocyclobutane rings), with a trace amount of 1,2-bis(3'-[2"-[3"'-trifluoromethylphenoxy]hexafluorocyclobutyloxy]phenyl)
25 hexafluorocyclobutyl ether (having three perfluorocyclobutane rings). By vacuum distillation two fractions were collected.

The first fraction contained primarily mono-
30 perfluorocyclobutane material consisting of two isomers (cis and trans 1,2-substituted hexafluorocyclobutane) with similar mass spectra (given for one isomer only): m/e: 484 (20.2%); 465 (12.9%); 273 (29.2%); 242 (30.1%); 207 (11.2%); 195 (13.0%); 145 (100.0%).

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The second fraction contained predominantly di-perfluorocyclobutane material, consisting mainly of three isomers (cis-cis, cis-trans, and trans-trans) of 1,2-substituted hexafluorocyclobutanes, and small amounts of four isomers of a product containing one 1,2-substituted hexafluorocyclobutane ring and one 1,3-substituted hexafluorocyclobutane ring (cis-1,2 cis-1,3; cis-1,2 trans-1,3; trans-1,2 cis-1,3; and trans-1,2 trans-1,3). All seven products gave roughly the same peaks in their mass spectra in differing intensities. The following mass spectral data was for the first product isomer to elute from the gas chromatography (GC) column, and corresponded to one of the three main isomers of two perfluorocyclobutane rings: m/e:

754 (36.4%); 593 (12.5%); 492 (14.1%); 415 (21.9%); 273 (27.7%); 242 (39.1%); 195 (21.5%); 173 (23.4%); 145 (100.0%); 126 (28.5%); 95 (23.1%); 92 (34.7%); 76 (57.6%); 64 (27.3%).

The second fraction also contained a small amount of material containing three perfluorocyclobutane rings, consisting of six isomers (cis-cis-cis, cis-cis-trans, cis-trans-cis, cis-trans-trans, trans-cis-trans, and trans-trans-trans) of 1,2-substituted hexafluorocyclobutanes. Because of the small amount of this product present in the mixture, the corresponding products containing one or more 1,3-substituted hexafluorocyclobutane rings were not detected. The mass spectra of the six isomers showed roughly the same peaks in slightly differing intensities. The following mass spectral data was from the first product isomer of tri-perfluorocyclobutane material to elute from the GC column: m/e: 1024 (21.6%); 593 (16.3%); 492 (35.5%); 415 (17.6%); 281 (16.2%); 273 (16.4%); 242 (26.0%);

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208 (15.9%); 207 (71.9%); 145 (100.0%); 92 (19.7%);
76 (26.8%).

5 In all cases, the primary products of
cyclization were 1,2-substituted hexafluorocyclobutanes,
with small amounts (1 to 2 percent) of 1,3-substituted
hexafluorocyclobutanes observable by GC/MS, (except for
the tri-perfluorocyclobutane material, of which only
trace amounts were seen) the two being distinguished by
10 a small peak at $m/e = 100$, corresponding to a fragment
of $CF_2=CF_2$ present in the mass spectra of the
1,2-substituted hexafluorocyclobutanes which was absent
in the 1,3-substituted products. Absolute
configurations of the different isomers were not
15 assigned.

This example shows that a compound containing
one trifluorovinyl group can be combined with a compound
containing two trifluorovinyl groups, the mixture then
20 being heated to cause cyclization of the trifluorovinyl
groups to provide a fluid containing
perfluorocyclobutane groups. Such fluids are of the
type useful as low dielectric hydraulic fluids or
25 lubricants.

30

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EXAMPLE 16: PREPARATION OF A FLUID POLYMER OF
1,3-BIS(TRIFLUOROVINYLOXY)BENZENE,
3-(1',1',2',2',TETRAFLUROETHOXY)-
TRIFLUOROVINYLOXYBENZENE AND 1,3-BIS(1',1',2',2'-
-TETRAFLUROETHOXY)BENZENE

A mixture (25 mL) consisting of 1,3-bis(trifluorovinyloxy)benzene (as prepared in Example 4) (26 percent), 3-(1',1',2',2',tetrafluoroethoxy)-trifluorovinyloxybenzene (54 percent), 1,3-bis(1',1',2',2'-tetrafluoroethoxy)benzene (as isolated in Example 4) (15 percent), and tetraglyme (5 percent) was placed in a 100 mL round bottom flask and heated at reflux under nitrogen for 5 hours. The resulting viscous oil was checked by GC and was found to contain unreacted 1,3-bis(1',1',2',2',-tetrafluoroethoxy)benzene and tetraglyme, as well as mixtures of isomers of heavy components. After removal of the light, unreacted components, two fractions are cleanly separated by fractional distillation and each was analyzed by GC/MS.

The first fraction was found to contain primarily 1,2-bis(3'-[1",1",2",2"-tetrafluoroethoxy]-phenoxy)hexafluorocyclobutane as two isomers (cis and trans substituted hexafluorocyclobutane) followed by small amounts (1 to 2 percent each) of two 1,3-substituted hexafluorocyclobutane products (cis and trans), all having roughly similar mass spectra. The following was the mass spectral data for the first isomer to elute from the chromatography column, and corresponded to one of the 1,2-substituted isomers: m/e: 580 (25.8%); 371 (11.3%); 321 (12.5%); 290 (23.4%);

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270 (36.4%); 243 (69.9%); 193 (100.0%); 95 (96.4%);
92 (55.9%); 76 (26.7%); 64 (29.9%); 51 (21.9%).

5 The second fraction contained 1,3-bis(2'-[3"-
{1"',1"',2"',2"'-tetrafluoroethoxy}phenoxy]hexa-
fluorocyclobutyl)phenyl ether, primarily as three
isomers of 1,2-substituted hexafluorocyclobutanes with a
small amount of four isomers of the product with one
1,2-substituted and one 1,3-substituted
10 hexafluorocyclobutane ring. The seven isomers all gave
roughly the same peaks in their mass spectra in
differing intensities. The following mass spectral data
was for the first isomer to elute from the GC column,
and corresponded to one of the three main isomers of the
15 product: m/e: 850 (24.7%); 540 (24.2%); 371 (41.5%);
321 (12.9%); 301 (16.4%); 290 (33.9%); 270 (74.4%);
243 (63.9%); 207 (24.1%); 193 (86.7%); 173 (14.8%);
95 (100.0%); 92 (63.2%), 76 (71.8%)64 (32.6%);
51 (15.5%).

20

This example shows that a compound containing
one trifluorovinyl group may be combined with a compound
containing two trifluorovinyl groups in a solvent, the
25 resulting mixture being heated to cause cyclization of
the trifluorovinyl groups. Such fluids are of the type
useful as low dielectric hydraulic fluids or lubricants.

EXAMPLE 17: PREPARATION OF 2,5-BIS(2-
30 TRIFLUOROETHENYLOXY)HEXANE

Sodium hydride (16.5 g, 60 percent dispersion
in oil, 0.41 mole) was transferred to an oven dried 2 L
3-necked flask. Dry dimethyl formamide (DMF) (400 mL)
was added via syringe and the flask was fitted with a

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stirrer, thermometer, and septum. The mixture is stirred and cooled in an ice bath as 2,5-hexanediol (17.78 g, 0.15 mole) dissolved in 50 mL of dry DMF is added slowly via syringe. The septum was replaced with a pressure-equalizing addition funnel, and the mixture was stirred overnight. The mixture was cooled to -10°C to -15°C with a dry ice/ethylene glycol bath, and 1,2-dibromotetrafluoroethane (TFDBE) (60 mL, 0.5 mole) is added dropwise to the stirring mixture. The temperature of the reaction was maintained at -10°C to -8°C. After one equivalent had been added, foaming was observed, which was allowed to subside before addition of TFDBE was resumed. Some slight foaming was observed for the rest of the reaction. As the reaction approached completion, large amounts of solid precipitate, which redissolved when the reaction was allowed to warm to 10°C.

The reaction mixture was partitioned between hexane and water. The hexane layer was washed with additional water to remove residual DMF, dried over magnesium sulfate, and concentrated to yield 63.15 g of orange oil. Volatile products were removed by vacuum distillation to yield 36.12 g of colorless oil, which was then chromatographed on alumina with hexane to yield 19.23 g of 2,5-bis(2-bromotetrafluoroethoxy)hexane (26.9 percent yield) and 5.42 g of 2-(2-bromotetrafluoroethoxy)-5-(1,1,2,2-tetrafluoroethoxy)hexane as confirmed by ¹⁹F NMR, ¹H NMR and IR spectra of products. ¹⁹F NMR: (TFA) δ-10.2 (t, J=6 Hz), 8.8 (t, J=6 Hz) HNMR: (TMS) δ1.32 (d, 6H, J=6 Hz), 1.63-1.90 (m, 4H), 4.20-4.78 (m, 2H).

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Zinc (1.93 g, 30 mmole) and 2,5-bis(2-bromo-tetrafluoroethoxy)hexane (3.45 g, 7.25 mmole) are weighed into a dry 100 mL 3-necked flask. Dry glyme (25 mL) was added via syringe and the resulting mixture was stirred and heated to reflux under nitrogen for 5 hours. The mixture was partitioned between pentane and water. The pentane extracts are dried over magnesium sulfate and concentrated to yield 2.11 g of pale yellow oil. Infrared analysis of this oil indicated the presence of some carbonyl containing impurities. The oil was dissolved in pentane and flushed through a column of neutral alumina to yield, after concentration, 1.33 g (65.8 percent yield) of the desired product. The title product was identified by 19F NMR, 1H NMR, and IR spectra. 19F NMR: (TFA) 846.2 (ddd, J=90 Hz, J_{cis} = 78 Hz, J_{FH} = 2 Hz, OCF), 53.8 (d, J=78, =CF cis), 53.9 (d, J=90, =CF trans) HNMR: (TMS) 81.31 (d, J=6 Hz, 6H), 1.55-1.90 (m, 4H), 3.80-4.40 (m, 2H) IR: (CM-1) 1845 (CF=CF₂), 1290 (B,C-O), 1130 (B, C-O).

The material was analyzed by DSC, and exhibited an exotherm of 500 Joules per gram (J/g) at 107°C.

25

EXAMPLE 18: PREPARATION OF METHYL 4-(2-BROMO-TETRAFLUOROETHOXY)BENZOATE, ITS CONVERSION TO TO 4-TRIFLUOROETHENYLOXYBENZOIC ACID AND THE BENZOYL CHLORIDE, AND USE OF THE CHLORIDE TO CHAIN EXTEND POLYCARBONATE OLIGOMERS

30

Methyl 4-hydroxybenzoate (304.3 g, 2 mole) was dissolved in 800 mL of methanol and was converted to the potassium salt by the slow addition of potassium hydroxide (132.02 g, 2 mole, 85 percent purity). The

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resulting mixture was stirred and cooled as necessary to maintain the temperature below 50°C. The solvent was then removed by rotary evaporation and the crystalline salt was dried under vacuum overnight at 140°C.

- 5 The dried salt was allowed to cool and transferred to an oven dried 2-liter flask under nitrogen. The flask was fitted with a mechanical stirrer, thermometer, heating mantle, condenser and
- 10 pressure-equalizing addition funnel. Dry dimethylsulfoxide (DMSO) (550 g) was added and the mixture was stirred and warmed to 60°C as 1,2-
- 15 -dibromotetrafluoroethane (537 g, 2.06 mole) was added slowly. (No appreciable reaction was observed at lower temperatures.) Reaction temperature is maintained at 65°C to 70°C for two hours after addition is complete. The mixture was then heated to 90°C and allowed to cool overnight.
- 20 Product was isolated by extracting the mixture with 500 mL of water to remove salts and DMSO. The product separated as an orange oil which was washed with water to remove residual DMSO. (The upper aqueous layer
- 25 was extracted with methylene chloride, and the methylene chloride solution was evaporated to yield about 40 g of product which was added to the rest of the product prior to the water washes.) The product (623 g) was distilled at 85°C/0.3 mm Hg to yield 561 g of colorless oil,
- 30 85 percent yield. The product was identified by 19F NMR, 1H NMR, and IR spectra.

To form a salt suitable for formation of the perfluorovinyl ether, another sample of methyl 4-(2-bromotetrafluoroethoxy)benzoate (66.25 g, 0.2 mole)

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was weighed into a 4-necked 500 ml round-bottomed flask fitted with a condenser, thermometer, mechanical stirrer, and heating mantle. Methanol (300 mL) and sodium hydroxide (8.05 g, 0.2 mole) were added to form a mixture which was stirred and heated to reflux for three hours. A sodium carboxylate formed and began to precipitate early in the reaction and was gelled into an almost solid mass after 1.5 hours. The mass was allowed to settle overnight and the solvent was then removed by rotary evaporation.

The sodium carboxylate was dissolved in warm water. A warm solution of zinc acetate (26.35 g, 0.12 mole) in 40 mL of water was added to precipitate the carboxylate as the zinc salt. The salt slurry was then cooled, and the zinc salt was filtered from the solution and dried under vacuum to yield 65.6 g (94 percent yield).

The dried zinc salt was transferred to a dry 4-necked 500 mL round-bottomed flask containing zinc metal (10 mesh, 13.0 g, 0.198 mole). Dry glyme (160 mL) was added by a canula and the flask was fitted with a condenser, mechanical stirrer, and thermometer. The mixture was stirred and heated to reflux under nitrogen overnight. The mixture was acidified by the addition of 18 mL of concentrated HCl, concentrated by rotary evaporation, and then partitioned between methylene chloride and water. The methylene chloride solution of the acid was dried over magnesium sulfate, filtered and concentrated to yield 40.02 g of 4-trifluoroethenyloxybenzoic acid as white crystals (97.6 percent yield, melting point 139°C to 140°C). The product

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4-trifluoroethenyloxybenzoic acid was identified by ¹⁹F NMR, ¹H NMR, and IR spectra.

To form the 4-trifluoroethyloxybenzoyl chloride, 4-trifluoroethenyloxybenzoic acid (79.4 g, 0.36 mole) was transferred to a 1-liter round-bottomed flask. Dry methylene chloride (250 mL) was added, and the resulting mixture was stirred under nitrogen as oxalyl chloride (62.5 g, 0.49 mole) was added. The mixture was stirred overnight and then concentrated by rotary evaporation. The brown liquid was distilled at 60°C to 65°C/0.2 mmHg (26.6 Pa) to yield 82.94 g of colorless liquid (97.4 percent yield). The product was identified by ¹⁹F NMR, ¹H NMR, and IR spectra.

To cap an oligomer, a low molecular weight polycarbonate oligomer (2000 MW) terminated with bisphenol A groups (7.5 g, about 7.8×10^{-3} mole of phenolic OH) was weighed into a 100 mL flask with the trifluoroethenyloxybenzoyl chloride (1.84 g, 7.8×10^{-3} mole). Dichloromethane (30 mL) was added to dissolve the oligomer, and the mixture was stirred as triethylamine (0.81 g, 8×10^{-3} mole) was added via syringe. A fine white precipitate forms in the mixture almost immediately. Dichloromethane was added to dissolve the precipitate, forming a dichloromethane solution which was extracted with water to remove triethylamine hydrochloride. The dichloromethane solution was dried over 4A molecular sieves, and concentrated to yield 9.06 g (100 percent yield) of oligomer capped with trifluoroethenyloxy benzoyl groups. Structure was verified by ¹⁹F NMR (trifluorovinyl ether pattern), ¹H-NMR (2 protons of the aromatic benzoate were shifted downfield to 8-8.3 ppm from the aromatic

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polycarbonate protons), and FT-IR (C=O stretch at 1739 cm^{-1} , distinct from the C=O stretch of polycarbonate at 1774 cm^{-1}).

5 A sample of the capped oligomer was heated to 300°C in a DSC apparatus to effect chain extension. The sample was cooled and reheated to determine the Tg, which was observed at 140.4°C (representative of high molecular weight polycarbonate). For comparison, a
10 sample of the uncapped oligomer heated to 300°C, cooled, and reheated, exhibited a Tg of only 106.8°C. The increase of 33.6°C in the Tg was attributed to the production of high molecular weight polycarbonate through the thermal cyclodimerization of the
15 trifluorovinyl ether groups.

EXAMPLE 19: REACTION OF 4,4'-BIPHENOL AND
TRIFLUOROVINYLOXYBENZOYL CHLORIDE

20 Dihydroxybiphenyl (0.7888 g, 0.00423 mole) was placed in a dry 250 mL round bottom flask with a magnetic stirring bar. The flask was capped with a rubber septum. Dry methylene chloride (25 mL) and
25 trifluorovinylloxybenzoyl chloride as prepared in Example 18 (2.000 g, 0.00846 mole) were each added to the flask via syringe. The mixture was stirred as triethylamine (0.86 g, 0.0085 mole) was added dropwise. The mixture was stirred at room temperature for 2 hours, then
30 filtered. A white precipitate was obtained and washed several times with methylene chloride to remove residual triethylamine hydrochloride. A white crystalline product was obtained and had a melting point of 225°C to 228°C. Qualitative solubility tests indicated that this product was nearly insoluble in methylene chloride,

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acetone, acetonitrile, hexane, methanol, water and benzene, only slightly soluble in hot tetrahydrofuran, and moderately soluble in carbon tetrachloride.

5 Infrared analysis (using a potassium bromide KBr pellet) gave the following spectrum (reported in cm^{-1}): 1830, indicative of a trifluorovinyl group; 1723, indicative of a benzoate ester; 1600 and 1495, indicative of aryl carbon-carbon double bond; 1315 and 10 1267, indicative of carbon-fluorine bonds.

Thermal analysis (DSC) of the monomer indicated a crystalline melt beginning at 223°C, followed immediately by a slight exotherm as the monomer 15 underwent polymerization. A second scan of the sample showed no thermal activity up to and including 350°C.

The melted monomer exhibited possible liquid 20 crystalline behavior during its short lived melt phase. As viewed under a cross-polarized light microscope, the melted monomer phase (at 230°C) exhibited birefringence suggestive of liquid crystalline behavior, followed by rapid polymerization to a crystalline solid. This solid 25 did not melt, but underwent discoloration and apparent decomposition when heated in air at temperatures above 400°C.

30 EXAMPLE 20: PREPARATION OF POLYESTERS FROM 1,2-BIS(4-
-CHLOROFORMYLPHENOXY)HEXAFLUOROCYCLOBUTANE BY SOLUTION
POLYMERIZATION

Methyl p-hydroxybenzoate was converted to its potassium salt by reaction with a stoichiometric amount of potassium hydroxide in methanol. The salt was

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isolated by evaporation and dried under vacuum. The dried salt was slurried in an equal weight of dry dimethyl sulfoxide. The mixture was stirred and heated to about 50°C and a slight excess of 1,2-dibromotetrafluoroethane was added slowly. The reaction temperature was maintained at 60°C to 70°C. An efficient condenser was necessary to condense the dibromotetrafluoroethane. After addition was complete, the mixture was warmed for an additional hour, cooled and poured into an equal volume of water. The product (methyl 4-(2-bromotetrafluoroethoxy)benzoate) separated as a brown oil which was distilled under vacuum (85°C to 90°C, 0.3 mmHg (39.9 Pa)) to yield a colorless oil (85 to 95 percent yield).

The bromotetrafluoroethylether was dehalogenated by combining it with a stoichiometric amount of granular zinc in glyme and refluxing overnight. After removal of the glyme by evaporation, the product, methyl 4-trifluoroethenyloxybenzoate, was distilled under vacuum (85°C to 90°C/8-10 mmHg (1064 Pa to 1330 Pa), 85 to 100 percent yield).

The methyl 4-trifluoroethenyloxybenzoate was cyclodimerized by heating at 195°C for several hours. The dimerized product was isolated by distillation (135°C to 150°C/0.025 mmHg (2.3 Pa), 97 percent yield, with the remainder being unreacted vinyl compound). The overall yield from methyl p-hydroxybenzoate was 80 percent.

The dimer was saponified to the diacid with 2.1 molar equivalents of sodium hydroxide in methanol. Upon acidification with concentrated hydrochloric acid

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the diacid precipitates and was filtered from the liquid as an insoluble white powder with a melting point above 300°C. Yields were quantitative. The diacid was converted to the diacid chloride by slurring it in approximately a 6 molar equivalent of thionyl chloride and warming the mixture to 50°C to 75°C. The product diacid chloride was soluble in dichloromethane and was purified by dissolving the crude reaction product in dichloromethane and filtering the diacid chloride solution from unreacted diacid (which was insoluble). The product was identified by ¹⁹FNMR, ¹HNMR and infrared (IR) spectra. IR 1790, 1755 cm⁻¹ (C=O) no CO₂H absorption.

Bisphenol AP (1,1-bis(4-hydroxyphenyl)-1-phenyl ethane) (6.14 g, 21.1 mmole) was transferred to a dried resin kettle (a reaction vessel with a large top that clamps onto the vessel) along with 50 mL of dry dichloromethane. The mixture was stirred under nitrogen as triethylamine (5.9 mL, 42.2 mmole) was added via syringe. The solution was stirred and cooled in a water bath as a solution of 1,2-bis(4-chloroformylphenoxy)-hexafluorocyclobutane (10.0g, 21.1 mmole) in dichloromethane (50 mL) was added via syringe. The mixture was allowed to stir overnight under nitrogen to form a polymer in solution.

The polymer was then capped by adding 0.25 mL of 4-trifluoroethenyloxybenzoyl chloride (as prepared in Example 18) to the solution with stirring. The solution was diluted with 200 mL of dichloromethane and washed with water to remove triethylamine hydrochloride until a sample of the water washes added to a 5 percent silver nitrate solution produced no silver chloride

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precipitate. The polymer solution was then poured into a glass dish, and the dichloromethane was allowed to evaporate overnight, leaving a clear, tough film, which was dried under vacuum at 140°C and was weighed. (Yield=14.58 g, 99.9 percent)

5

EXAMPLE 21: PREPARATION OF POLYESTERS FROM 1,2-BIS(4-
-CHLOROFORMYLPHENOXY)HEXAFLUOROCYCLOBUTANE BY EMULSION
POLYMERIZATION

10

Bisphenol AP (10.51 g, 36 mmole) is transferred to a blender container along with water (200 mL), 50 percent aqueous sodium hydroxide (6.6 g, 82 mmole) and benzyltrimethylammonium chloride (2 g, 6.5 mmole, 15 60 percent aqueous solution). Agitation was supplied by a blender plugged into and having its speed controlled by a Variac. The mixture was agitated at 25 to 30 percent power until the bisphenol AP dissolves.

20

1,2-bis(4-chloroformylphenoxy)hexa-
fluorocyclobutane (prepared as in Example 20) (17.12 g, 36 mmole), was dissolved in 70 mL of dichloromethane to form a diacid chloride solution and was chilled in an ice bath. Dichloromethane (25 mL) was added to the 25 blender, which was agitated at 30 percent power for 2 minutes, at which time the chilled diacid chloride solution was added to the blender over a period of 20 seconds to form an admixture. The container in which 30 the diacid chloride mixture was chilled was rinsed with 30 mL of dichloromethane, which was added to the admixture. The admixture was agitated at 40 percent power for 12 minutes; then 1.2 mL of benzoyl chloride was added. The admixture was agitated for an additional 2 minutes. Then agitation was stopped and layers are

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allowed to separate. An aqueous layer was decanted, and a lower, dichloromethane layer, was agitated with 200 mL portions of deionized water until a sample of the water tested negatively for chloride ion.

5 Addition of an equal volume of isopropyl alcohol to the volume of dichloromethane layer precipitated a polymer from the dichloromethane solution as a thick, viscous mass. The polymer was allowed to
10 air dry, then redissolved in dichloromethane to form a clear solution and poured into a glass dish. Evaporation of the dichloromethane overnight yielded a tough clear film which was dried under vacuum at 140°C. Weight of recovered polymer was 24.56 g, 98 percent
15 yield.

EXAMPLES 22-27: POLYESTERS PREPARED USING 1,2-BIS(4-
-CHLOROFORMYLPHENOXY)HEXAFLUOROCYCLOBUTANE

20 The process of Example 20 for the solution preparations and the process of Example 21 for the emulsion preparations were repeated using the following bisphenols with the results indicated in the following
25 Table III, which includes polymers of Examples 20 and 21 for comparison:

30

Table III

Ex. No.	Bisphenol **	Yield (%)	Tg (°C)	Molecular Weight	ppPolymerization Method	Dielectric Constant/dissipation Factors at 1 KHz
22	Bisphenol A	100	137	47000	solution	2.93/0.0031
20	Bisphenol AP	99.9	178	60000	solution	3.05/0.0042
23	Bisphenol AF	97	160	66000	solution	2.94/0.0036
24	4,4'-Biphenol	98	>400	--	solution	*
25	Hydroquinone	99	>400	--	solution	*
26	Bisphenol A	100	--	64000	emulsion	--
21	Bisphenol AP	98	185	104000	emulsion	--
27	Bisphenol AF	100	--	79000	emulsion	--

* These materials were highly crystalline and precipitated from the reaction mixture. Molecular weights could not be determined by GPC due to insolubility.

**Bisphenol AF is 2,2-bis(4-hydroxyphenyl)-hexafluoropropane; bisphenol A is 2,2-bis(4-hydroxyphenyl)propane.

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Tensile and flexural strength were determined for a sample of the bisphenol A polymer prepared by solution polymerization (Example 22).

5 Tensile strength was 6460 pounds/square inch.

Flexural strength was 3060 pounds/square inch.

Flexural Modulus was 330,000 pounds/square inch.

10

EXAMPLE 28: POLYMERIZATION OF 1,2-BIS(4-
-ETHYNYLPHENOXY)HEXAFLUOROCYCLOBUTANE

15 p-Ethylphenol was dissolved in methanol to form an admixture. A methanolic solution of one equivalent of potassium hydroxide was added to the stirring admixture. The admixture was cooled to maintain a temperature below 40°C. Stirring and cooling was
20 maintained for about 15 minutes after addition was complete.

The methanol was then removed by rotary evaporation and a resulting wet salt was transferred to
25 a suitable container and dried under vacuum at 100°C to 140°C to produce a dry salt. The dry salt was transferred to a dry flask and an equal volume of dry DMSO was added to form a slurry. The flask was fitted with a mechanical stirrer, thermometer, efficient
30 condenser, and pressure-equalizing addition funnel.

The salt slurry was stirred and cooled to less than 20°C as a slight excess (1.1 equivalents) of 1,2-dibromotetrafluoroethane is added slowly. The

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reaction was heated to 60°C for about 2 hours after addition was complete.

5 The 2-bromotetrafluoroethyl ether was isolated by pouring into an equal volume of water. The ether separated as a lower layer of oil and was purified by vacuum distillation.

10 4-Trifluorovinyl-1-ethylbenzene was synthesized by combining the 2-bromotetrafluoroethyl ether with granular zinc in dry glyme and refluxing at 85°C to 90°C with stirring overnight.

15 After completion of the reaction, the precipitated zinc salts were removed by centrifugation. The glyme was removed by rotary evaporation and the product, 4-trifluorovinyl-1-ethylbenzene, was purified by vacuum distillation.

20 4-Trifluorovinyl-1-ethylbenzene was cyclodimerized by heating to 180°C to 195°C for 8 hours. Low boiling impurities and unreacted perfluorovinyl compound were removed by vacuum distillation. The product 1,2-bis(4-ethylphenoxy)hexafluorocyclobutane was
25 distilled under vacuum (110°C/0.05 mmHg (6.6 Pa)) 40 percent yield from 4-ethylphenol.

30 A 5 g sample of 1,2-bis(4-ethynylphenoxy)hexafluorocyclobutane (as prepared in Example 20) was thermally cured at 180°C for 3 hour followed by a postcure at 250°C for 30 minutes. The density of the polymer was 1.34 g/cc. Dielectric constant was 2.6 at 1 KHz.

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DSC analysis of 1,2-bis(4-ethynylphenoxy) hexafluorocyclobutane indicated a broad exotherm starting at 160°C and ending at 280°C with $\Delta H = 632$ Joules/g. The initially colorless oil turned into a clear, dark red solid which was analyzed by DSC, TMA, and TGA (Thermogravimetric analysis). TGA (20°C/min., nitrogen sweep) of the cured sample shows: 2 percent loss at 400°C, 5 percent loss at 470°C, 35 percent loss at 580°C, and 80 percent loss at 900°C. No Tg was observed up to 350°C by DSC or TMA.

EXAMPLE 29: SYNTHESIS AND POLYMERIZATION OF 1,1,1-
-TRIS(4-TRIFLUOROETHENYLOXYPHENYL)ETHANE

Potassium hydroxide (678.72 g, 10.28 mole, 85 percent) was dissolved with cooling into 630 mL of water in a 5 liter round-bottomed flask fitted with a thermometer and stirrer. Methanol (400 mL) was added and the mixture was stirred under nitrogen in an ice bath as a solution of THPE [1,1,1-tris(4-hydroxyphenyl)ethane] (1051 g, 3.43 mole) in 1650 mL of warm methanol (40°C) was added. Methanol was then removed from the resulting solution of the potassium salt of THPE in water/methanol by distillation under reduced pressure (140 mm Hg, 55°C to 60°C) with addition of a total of 1245 mL of water to make up for losses and to obtain a solution of THPE potassium salt in water with the consistency of light syrup. The potassium salt of THPE was isolated by evaporation of this water solution (48 percent solids by weight) in a drum dryer. The resulting dried THPE salt contained about 4 percent water by weight.

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The dried THPE salt was transferred to a 12 L round-bottomed flask fitted with a condenser and water trap along with 5 L of dimethylsulfoxide (DMSO) and 1.5 L of toluene. This slurry was stirred and heated to reflux under nitrogen to remove residual water by azeotroping it with toluene. After 6 hours of reflux no further water collection was seen in the water trap and the water trap was replaced with a Soxhlet extractor containing dry sodium sulfate. The mixture was refluxed through the Soxhlet extractor for a total of 5.5 h with the sodium sulfate being replaced with an equivalent amount of dry sodium sulfate once at the halfway point, during this process. About 1 L of toluene was then removed by distillation and the remaining mixture was cooled to 18°C by means of an internal cooling coil containing either tap water or chilled glycol as needed. The temperature of the stirring mixture was maintained at 16°C to 18°C by means of this internal cooling coil as 1,2-dibromotetrafluoroethane (3000 g, 11.54 mole, 1382 mL) was added over 1 hour and the resulting mixture was stirred at 18°C for 36 hours.

The reaction was worked up by pouring the mixture into an equal volume of cold water with stirring and then allowing the layers to separate. The lower layer containing the product was drained and the upper aqueous layer was washed with hexane. The hexane wash was combined with the product layer and evaporated under reduced pressure to remove solvents. The crude product solidified into a crystalline mass melting at ca. 100°C. This mass was melted and distilled at reduced pressure (190°C to 195°C, 0.05 mm Hg) to yield the product, 1,1,1-tris(4-(2-bromotetrafluoroethoxy)phenyl)ethane, as a yellowish viscous oil which crystallizes upon standing.

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The yield of this reaction was 88.1 percent and the product was 93 percent pure with the remaining 7 percent being the byproduct 1,1-bis(4-(2-bromotetrafluoroethoxy)phenyl)-1-(4-(1,1,2,2-tetrafluoroethoxy)phenyl)ethane which resulted from the replacement of one of the bromine atoms of the product with a hydrogen atom. The byproduct may be removed by melting the distilled crystalline mass and pouring it into an equal volume of methanol with stirring. The product preferentially crystallizes into fluffy white needles which can be filtered from the methanol solution. Alternatively, the 93 percent pure product may be used directly in the dehalogenation reaction.

The crystalline 1,1,1-tris(4-(2-bromotetrafluoroethoxy)phenyl)ethane is found to have the following properties:

White needles, melting point 110°C;

F-19 NMR: δ -10.4 (t, J = 6 Hz, which is attributed to $-\text{CF}_2\text{Br}$), 7.5 (t, J = 6 Hz, which is attributed to OCF_2);

H-NMR: δ 2.2 (bs, 3 H), 7.1 (bs, 12 H); and

IR: cm^{-1} 1501, 1329, 1312, 1206, 1173, 1126, 1100, 1012, 929, 784.

Granular zinc (213.3 g, 3.26 mole, 10-20 mesh) was weighed into an oven-dried 3 L round-bottomed flask. The flask was then fitted with a stirrer, thermometer, septum, and a 1 L pressure-equalizing addition funnel containing 1,1,1-tris(4-(2-

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bromotetrafluoroethoxy)phenyl)ethane (833.7 g, .989 mole, 97 percent purity). Dry diglyme (1045 g, 1115 mL) was added to the flask via canula and also to the addition funnel (384 g, 410 mL). The septum was replaced with a stopper, and the zinc/diglyme slurry was stirred and heated to 115°C as the contents of the addition funnel were heated by means of heating tape to ca. 80°C to form a homogeneous solution. The solution of 1,1,1-tris(4-(2-bromotetrafluoroethoxy)phenyl)ethane in diglyme was added slowly to the hot stirring zinc/diglyme slurry over 2 h, maintaining the reaction temperature at 115°C to 125°C by varying both heating rate and rate of addition. After addition was complete the mixture, which now contains precipitated zinc salts, was heated at 120°C to 125°C for an additional 5 h. The mixture was allowed to cool and the precipitated zinc salts were removed by centrifugation. Ethyl acetate was used to rinse the flask.

The resulting diglyme solution of the tris-perfluorovinyl ether product, 1,1,1-tris(4-trifluoroethenyloxyphenyl)ethane, was concentrated under reduced pressure by rotary evaporation and the resulting mixture of product and zinc salts was slurried in hexane and flushed through a 6 inch by 6 inch column of neutral alumina commercially available from Aldrich Chemical Company under the trade designation Brockmann I. The product was isolated by evaporation of the hexane solution under reduced pressure. The product was isolated as a colorless oil (85 to 90 percent yield, 89 to 79 percent purity). The remainder of the material (7 to 10 percent) was a bis-perfluorovinyl ether,

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1,1-bis(4-trifluoroethenyloxy)phenyl)-1-(4-(1,1,2,2-tetrafluoroethoxyphenyl)ethane.

The bis-perfluorovinyl ether was removed by
countercurrent extraction to obtain up to 99.9 percent
5 pure tris-perfluorovinyl ether. Some solvent mixtures
suitable for the separation were hexane/acetonitrile,
hexane/dimethyl sulfoxide, and hexane/dimethylformamide.
A countercurrent extractor was constructed from PFA
10 (perfluoroalkoxy) tubing (1 inch inside diameter, 4 feet
length) packed with stainless steel packing,
commercially available from Metex Corp. under the trade
designation Goodloe™, two electronic pumps commercially
available from Pennwalt Corp. under the trade
15 designation CHEMPULSE™ (Pennwalt model #45-050/K1M),
two solvent reservoirs filled respectively with mutually
saturated hexane and acetonitrile, and two receivers.

A sample of impure tris-perfluorovinyl ether
20 (180.8 g, 93.5 percent tris-, 6.5 percent bis-
perfluorovinyl ether; purity as determined by gas
chromatography corresponding to mole percent) was
diluted with 1500 mL of hexane to make an approximately
25 10 percent (by volume) solution. The pumps were
started, with hexane pumped into the bottom of the
column (above the acetonitrile take-off) and
acetonitrile pumped into the top of the column (below
the hexane take-off). The flow rates were adjusted to
30 90 mL/minute for hexane and 45 mL/minute for
acetonitrile. The hexane reservoir was allowed to drain
until nearly empty, and the solution of impure tris-
perfluorovinyl ether was transferred to the reservoir.
After this was transferred onto the column, the
reservoir was filled again with 1500 mL of hexane

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(saturated with acetonitrile). This was allowed to pump through the column and into the product reservoir to ensure complete washing of the product from the column. The hexane solution which exited the column contained tris-perfluorovinyl ether (99.5 percent purity, 5 49 percent recovery). The acetonitrile solution which exited the column contained the remainder of the product (88.35 g, 85.5 percent tris- and 14.5 percent bis-perfluorovinyl ether) and was concentrated by rotary 10 evaporation, rediluted in hexane (750 mL) and purified by running it through the countercurrent extractor to give 50.55 g of tris-perfluorovinyl ether (98.2 percent purity). The acetonitrile solution from this pass 15 contained 25.7 g of material which was 71 percent tris and 28.5 percent bis-perfluorovinyl ether. The ether was found to have the following properties:

1,1,1-tris(4-trifluoroethenyloxyphenyl)ethane:

20 Colorless, mobile oil

F-19 NMR: delta 42.7 (dd, J(cis)= 60 Hz, J(gem)= 100 Hz, which was attributed to =CF (terminal vinyl fluorine), 25 cis to F 49.3 (dd, J(trans)= 120 Hz, J(gem)= 100 Hz, which was attributed to =CF, trans to F 55.3 (dd, J(cis)= 60 Hz J(trans)= 120 Hz, which was attributed to OCF groups);

30 H-NMR: delta 2.1 (bs, 3 H), 6.95 (bs, 12 H); and

IR: cm-1 1830 which was attributed to (CF=CF₂) groups, 1500, 1313, 1273, 1205, 11781, 1138, 1011.

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The 1,1,1-tris(4-trifluoroethenyloxyphenyl)ethane polymerized at 140°C to 350°C, with a peak exotherm at 235°C as determined by differential scanning calorimetry (DSC).

5

A polymer was prepared by degassing a 9 g sample of the 93.5 percent pure product obtained before purification. 1,1,1-tris(4-trifluoroethenyloxyphenyl)ethane under vacuum until no visible bubbles form at room temperature; then heating the sample to 150°C to 160°C for 2 hours, then followed by heating at 240°C for 30 minutes. The sample was then allowed to cool to room temperature. The sample was a solid which was then chipped out of its container and ground into a powder using mortar and pestle. The powder was poured into a mold measuring about 4 by 5 by 1/32 inches (10.2 by 12.7 by 0.008 cm), put in a press, and compression molded at 240°C and 10,000 psig (pounds per square inch on the gauge) for 15 minutes. A resulting plaque was removed without cooling and was observed to be clear, flexible and colorless.

The polymer was found to have a Tg of 282.1°C as measured by thermomechanical analysis (TMA) on a mettler TA 3000

EXAMPLE 30: POLYMERIZATION OF 1,1,1-TRIS(4-
-TRIFLUOROETHENYLOXYPHENYL) ETHANE

30

A 30 g sample of the material prepared in Example 29 which is 99.5 percent pure 1,1,1-tris(4-trifluoroethenyloxyphenyl) ethane is filtered and poured into a vertical casting mold measuring 3 by 4 by 1/8 inches (7.6X10.2X0.3cm). The mold was placed in a

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vacuum oven at 140°C to 160°C for a period of 2 hours after which, the heat was increased to 240°C to 250°C for a period of 1 hour. The heat was turned off and the mold allowed to cool to room temperature. The molded polymer was removed and found to have the following properties:

Colorless, transparent, Tg (as measured by Thermomechanical Analysis on a Mettler TA 3000) = 300°C; Dielectric Constant (as measured by the procedure of ASTM D150-87) = 2.45 (1 MHz) Dissipation Factor (as measured by the procedure of ASTM D150-87) = 0.0005 (1 MHz). Upon postcuring by heating twice from 250°C to 360°C at a rate of 10°C per minute; a Tg of 414°C was obtained.

EXAMPLE 31: POLYMERIZATION OF 1,1,1-TRIS(4-TRIFLUOROETHENYLOXYPHENYL) ETHANE

The procedure of Example 29 was repeated obtaining samples of 1,1,1-tris(4-trifluoroethenyloxyphenyl) ethane having a purity of 97 mole percent after having been flushed through alumina using hexane.

A sample of the 9 percent pure 1,1,1-tris(4-trifluoroethenyloxyphenyl) ethane was poured into a compression mold and heated to 160°C for a period of 2 hours then 240°C for a period of 30 minutes, after which it was cooled to 25°C and removed from the mold. The resulting polymer was found to have a Tg of 286.1°C and a dielectric constant (as measured by the procedure of ASTM D15D-87) of 2.55 and dissipation factor (as

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measured by the procedure of ASTM D15D-87) of 0.001 (1 Mega Hertz (MHz)).

EXAMPLE 32: POLYMERIZATION OF 1,1,1-TRIS(4-
-TRIFLUOROETHENYLOXYPHENYL) ETHANE

5

The procedure of Example 29 is repeated obtaining samples of 1,1,1-tris(4-trifluoroethenyl-oxyphenyl) ethane having the following purities after the indicated steps:

10

Table IV

Step No.	Step	purity (mole percent*)	Tg°C
6	catalyst and solvent (hexane) removal	89.6	276
7	counter current extraction using hexane/ acetonitrile, first cut in hexane	99.8	300
8	recover* from acetonitrile without further purification	73.6	242
9	acetonitrile sample after purification by second extraction in hexane	85.7	251
10	recovery from acetonitrile extraction of step 8	50	178

*as determined by gas chromatography

A sample of each of the above materials were poured into a pan and put into a vacuum oven at 140°C for a period of 2 hours, after which the temperature was raised to 240°C for a period of 1 hour. The pan was removed from the oven and the resulting polymer was cooled to room temperature and removed from the pan. Using TMA using a Mettler TA 3000 system, the samples were found to have the Tg's indicated in Table IV.

30

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5 The samples of steps 8 and 10 were observed to soften indicative of thermoplastic character, and the samples of steps 6, 7 and 9 were observed to undergo a change in rate of expansion indicative of thermoset character.

10 These examples show that various purities of tris-perfluorovinyl monomers are obtained using various purification methods and that Tg increases with percentage of polyfunctional monomer. Counter current extraction is particularly useful for removing such impurities as bis-perfluorovinyl ethers. With such extractions, tris-perfluorovinyl monomers exceeding 15 99.9 percent in purity are obtained and are particularly useful, for instance in electronics uses. Generally such counter current solvent extractions require two solvents which are substantially immiscible one of which preferentially dissolves the desired product. Solvent 20 combinations useful for the separation useful in the practice of the present invention include solvents for the desired monomer paired with solvents in which the monomer is less soluble, but at least some of the impurities are more soluble. Such solvent pairs include 25 hexane/acetonitrile, hexane/dimethylsulfoxide, and hexane/dimethylformamide.

30 Alternatively, the monomers are suitable for polymerization after preparation without purification, preferably with removal of solvent(s) used in preparation. Such monomers in combination with by-products of their preparation are suitable, for instance, for applications wherein lower Tg's are suitable such as objects.

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EXAMPLE 33: CROSSLINKING OF 4,4'-
-BIS(TRIFLUOROVINYLOXY)BIPHENYL

After the preparation and polymerization of
5 4,4-bis(trifluorovinyloxy) biphenol in Example 1 and 2,
a sample plaque of the biphenyl perfluorocyclobutyl
ether polymer (12 cm x 8 cm x 1 cm) was placed inside a
baking dish in a vacuum drying oven and was cured under
vacuum at 310°C for 20 hours. The sample was removed
10 and a coupon was cut (6.0 cm x 1.2 cm x 0.33 cm) for
dynamic mechanical analysis. The analysis showed a Tg
of 175°C with no complete melt occurring, as was
evidenced by maintenance of a storage modulus up to and
including 344°C. This cured (crosslinked) polymer also
15 did not dissolve in THF but swelled into a gel.

A sample of the thermoplastic biphenyl
perfluorocyclobutyl ether polymer was placed in a
20 Rheometrics RMS-605 Mechanical Spectrometer using 25 mm
parallel plates with a 1 mm gap. Using a 10 percent
strain, storage and loss moduli were measured from
0.1 to 100 radians per second, measuring ten different
frequencies per decade of frequency, every 15 minutes.
25 Isothermal measurements were carried out according to
the technique of H.H. Winter and F. Chambon,
J. Rheology, 30(2), 367-382 (1986) except that the gel
points were measured at 320°C and 360°C. The log of tan
delta (G''/G'), that was the logarithm of the ratio of
30 the loss modulus (G'') to the storage modulus (G'), was
plotted against time for various frequencies. A gel
point was indicated by convergence of the various
frequency dependent tan deltas in the plot at
15 minutes. A second experiment was run under similar
conditions, but at 320°C isothermal; a plot of tan delta

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against time indicated a gel point at 80 minutes. Furthermore, samples after being heated beyond the gel points were not soluble in tetrahydrofuran. Thus, the system appears to crosslink in 15 minutes at 360°C and in 80 minutes at 320°C. Crosslinked samples exhibited some reddish brown or yellow color.

Physical property determinations on samples of the thermoplastic (uncrosslinked) polymer and on the crosslinked polymer showed significant differences as indicated in Table V below:

Table V
Physical Property Comparison

	Thermoplastic Polymer	Crosslinked Polymer
Tensile Strength ¹	5,500 psi	7,200 psi
Tensile Modulus ¹	200,000 psi	255,000 psi
Percent Elongation ¹	12 %	4%
Flexural Strength ²	10,800 psi	8,700 psi
Flexural Modulus ²	234,000 psi	315,000 psi
Dielectric Constant ³	2.57 (10kHz)	2.59 (10 kHz)
Dissipation Factor ³	0.0004 (10 kHz)	0.0006 (10 kHz)

1. As determined by the procedures of ASTM D882-83.
2. As determined by the procedures of ASTM D790-81.
3. As determined by the procedures of ASTM D150-87.

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The data in Table V shows that crosslinking increases tensile strength and modulus as well as flexural modulus while reducing elongation without substantial change in electrical properties.

5

EXAMPLE 34: CROSSLINKING OF 9,9-BIS(4'-TRIFLUOROVINYLOXY)PHENYL)FUORENE

After preparation and polymerization of 9,9-bis(4'[(trifluorovinyloxy)phenyl]fluorene, as in Example 3, a sample of the 9,9-bis(4'-oxyphenyl)fluorene perfluorocyclobutyl ether polymer was placed in the Rheometrics RMS-605 Mechanical Spectrometer using the conditions of Example 33. A plot of the tan delta against time for a 360°C isothermal experiment indicated a gel point in less than 10 minutes. A similarly run experiment at 320°C isothermal indicated a gel point in 35 minutes.

20

These gel points were indicative of curing of the samples into crosslinked polymer systems. Thus, the system appeared to crosslink in less than 10 minutes at 360°C and in 35 minutes at 320°C. Samples of the polymer heated to the gel point were insoluble in acetone, dichloromethane and tetrahydrofuran. The Tg was measured by differential scanning calorimetry to be 240°C.

30

EXAMPLE 35: PREPARATION, POLYMERIZATION AND CURING OF 2,2-BIS((4-PERFLUOROVINYLOXY)PHENYL)PROPANE

The procedure for preparing the diperfluorovinyl compound of Example 1 was followed except that smaller scale equipment was used with about

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half the amounts of solvent for the various steps using 100.0 g, 0.44 mole of para-bisphenol A in place of the 4,4'-dihydroxybiphenyl; 59.0 g, 0.89 mole of potassium hydroxide pellets; 240 g, 0.92 mole of 1,2-dibromotetrafluoroethane; and 25.0 g, 0.38 mole of granular zinc. The toluene mixture was heated to reflux (125°C). Water was removed by azeotropic distillation for a total of 48 hours, without cooling after 24 hours. Before addition of the 1,2-dibromotetrafluoroethane, the toluene was dried by refluxing through the extractor for 20 hours. After cooling to room temperature the reaction flask was cooled to 18°C in an ice bath. The 1,2-dibromotetrafluoroethane was added at a rate that maintained a reaction temperature of 18°C to 22°C. Then the mixture was allowed to warm to room temperature, and was heated slowly to 50°C and stirred at 50°C for 6 hours.

A crude reaction mixture formed and was filtered. The filtrate was evaporated thoroughly leaving a residue which was chromatographed on neutral alumina (50 to 200 mesh) using hexane as eluent to provide 113.9 g (44 percent yield) of a product having a GC/MS with peaks at the following mass to charge ratios (m/e): 587 (4.6%); 585 (9.2%); 583 (5.0%); 572 (44.5%); 570 (100%); 568 (52.0%); 397 (11.3%); 395 (11.0%); 315 (27.1%); 313 (28.2%); 299 (28.0%); 297 (30.4%); 181 (31.1%), 179 (37.6%); 167 (29.1%); 165 (37.8%); 131 (33.6%); 129 (36.9%); 115 (32.4%); 101 (35.7%); 91 (31.3%); 77(33.5%) consistent with a bisphenol A bis(2-bromotetrafluoroethyl) ether, 99+ percent pure by GC/MS analysis.

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After reaction with the granular zinc at 105°C, the bisphenol A bis(2-bromotetrafluoroethyl) ether (103.4 g, 0.176 mole) was placed in a 100 mL dropping addition funnel and added at a rate that maintained a reaction temperature of 105°C to 108°C. When the addition was complete the mixture was stirred at 108°C for 2.5 hours, then cooled to room temperature. The mixture was centrifuged to remove the solids; the precipitate was separated and washed with acetone and again separated by centrifuging. The liquid portions were combined and evaporated leaving a residue which was chromatographed through a neutral alumina column using hexane as an eluent to provide 42.8 g (63 percent yield) of a product having a GC/MS with peaks at the following mass to charge ratios (m/e): 388 (17.5%); 374 (20.0%); 373 (100%); 276 (30.4%); 215 (46.7%); 199 (12.8%); 179 (24.8%); 178 (50.0%); 152 (15.6%); 118 (24.0%); 117 (18.3%); 115 (17.1%); 102 (19.9%); 89 (23.5%); 77 (22.6%); 76 (29.9%) bisphenol A bis(trifluorovinyl) ether.

The bisphenol A bis(trifluorovinyl) ether monomer (13.6 g) was combined with 14.0 mL of Multifluor™ APF 215 solvent in a 100 mL 3-necked round bottom flask fitted with a mechanical stirrer and a nitrogen padded reflux condenser. Stirring was begun as the mixture was heated to reflux. The mixture was stirred at reflux for 5 hours, then allowed to cool to room temperature. A layer of polymer phase-separates to the top of the solvent. This polymer was removed and evaporated at 180°C under high vacuum (0.15 mmHg (19.9 Pa) to remove residual solvent.

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A sample of the polymer was placed in the Rheometrics RMS-605 Mechanical Spectrometer using the conditions used in Example 33. A plot of the tan delta against time for a 360°C isothermal experiment indicated a gel point in 50 minutes. A similar experiment at
5 320°C isothermal indicated that no gel point was reached by this polymer in the 150 minute time span of the experiment. These rheological experiments indicate that crosslinking of this polymer was much slower.

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CLAIMS :

1. A process for preparing a polymer having perfluorocyclobutane rings comprising the steps of:
 - (a) contacting monomers having at least two dimerizable perfluorovinyl groups; and
 - (b) exposing the monomers to heat such that a polymer containing perfluorocyclobutane rings is formed.
2. The process of Claim 1 wherein the monomers are heated to a temperature of at least about 40°C.
3. The process of Claim 1 wherein the monomers have at least one atom between the dimerizable perfluorovinyl groups.
4. The process of Claim 3 wherein the atom is oxygen or sulfur and the monomers have at least one aromatic molecular fragment having from 6 to 50 carbon atoms.
5. The process of Claim 4 wherein the aromatic molecular fragment has more than one aromatic ring.
6. The process of Claim 5 wherein the aromatic molecular fragment is 4,4'-biphenylene; phenylene; 9,9-diphenylfluorene; oxydiphenylene; thiodyphenylene; 2,2-diphenylenepropane;

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1,1,1,3,3,3-hexafluoro-2,2-diphenylenepropane; 1,1-diphenylene-1-phenylethane 1,1,1-triphenyleneethane; 1,3,5-triphenylenebenzene; 1,3,5-(2-phenylene-2-propyl)benzene; 1,1,1-triphenylenemethane; 1,1,2,2-tetraphenylene-1,2-diphenylethane; bis(1,1-diphenyleneethyl)benzene; 1-(2-phenylene-2-propyl)-4-(1,1-diphenyleneethyl)-benzene; 2,2-diphenylene propane; 2,2'-diphenylene, 1,1,1,3,3,3-hexafluoropropane; 1,1-diphenylene-1-phenylethane; naphthalene; or anthracene.

7. The process of Claim 1 wherein the polymer is linear.

8. The process of Claim 7 wherein the polymer has a molecular weight of at least about 10,000.

9. The process of Claim 1 wherein the monomer is an oligomer having perfluorovinyl end groups.

10. The process of Claim 9 wherein the oligomer is a polyether; poly(carboxylic acid derivative); polysulfone; polycarbonate; polyimide; polyamide, polyamide-polyimides; liquid crystal polymer or mixtures thereof.

11. The process of Claim 10 wherein the perfluorovinyl group is a perfluorovinyl aromatic ether.

12. The process of Claim 1 wherein at least one monomer is a perfluoroalkyl diperfluorovinylether compound.

13. The process of Claim 12 wherein the monomer has from 5 to 14 carbon atoms and the resulting polymer has a molecular weight of at least about 10,000.

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14. A polymer having a backbone comprising hydrocarbyl groups, perfluorocyclobutane rings and non-carbon atoms.

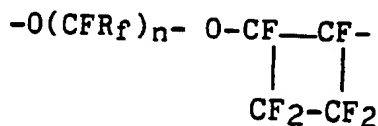
5 15. The polymer of Claim 14 wherein the hydrocarbyl group is aromatic.

16. The polymer of Claim 15 wherein the non-carbon atoms are oxygen or sulfur.

10 17. The polymer of Claim 16 which has a Tg of at least about 25°C.

18. A polymer having repeating units represented by the following formula:

15



20

wherein the polymer has an average molecular weight of at least about 10,000 and wherein R_f is a branched fluoroalkyl, a linear fluoroalkyl or fluorine and n is 1 to 10.

25

19. The process of Claim 1 wherein at least about 0.5 mole percent of the monomers have at least three dimerizable perfluorovinyl groups.

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20. The process of Claim 19 wherein the monomers are heated to a first temperature to increase viscosity of the monomers, then heated to a second higher temperature to result in a crosslinked polymer.

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21. The process of Claim 20 wherein the first temperature is from 50°C to 400°C and the second temperature is from 100°C to 450°C.

5 22. The process for of Claim 1 wherein the monomers in step (a) have two dimerizable perfluorovinyl groups.

23. A process for preparing a crosslinked polymer having perfluorocyclobutane rings comprising the steps of:

- (a) contacting monomers having two dimerizable perfluorovinyl groups;
- 15 (b) exposing the monomers to heat and that a polymer containing perfluorocyclobutane rings is formed; and
- (c) exposing the polymer to crosslinking initiating means such that crosslinking occurs and a crosslinked polymer is produced.

24. The process of Claim 23 wherein the crosslinking initiating means is a means of providing free radicals.

25 25. The process of Claim 24 wherein the crosslinking takes place substantially without addition of a crosslinking agent or catalyst.

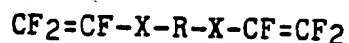
30 26. The process of Claim 4 wherein the crosslinking initiating means is wave energy or heat including radiant heat.

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27. The process of Claim 26 wherein the crosslinking step takes place at a temperature at least about 50°C higher than the temperature used in step (b).

5 28. The process of Claim 27 wherein the crosslinking step (c) takes place in a shaping apparatus.

29. The process of Claim 28 wherein the monomers have a structure represented by Formula I:
10



wherein R represents an unsubstituted or inertly substituted hydrocarbyl group which reacts with
15 perfluorovinyl groups residual in a substantially linear polymer to form a crosslinked or branched molecular structure; and each X is independently selected from the group consisting of groups having at least one
20 non-carbon atom between R and -CF=CF₂.

30. The process of Claim 29 wherein R includes a structure having at least two multiple bonds separated by a single bond and wherein each X is independently an
25 oxygen atom, a sulfur atom, a sulfoxide group, a sulfone group, a carbonyl group, and a thiocarbonyl group or a silanediyl group.



31. The process of Claim 19 wherein from 75 to
30 100 mole percent of the monomers have at least three dimerizable perfluorovinyl groups.

32. A polymer prepared by the process of Claim 23.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 90/03151

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC ⁵ : C 08 F 16/32		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
IPC ⁵	C 08 F	
Documentation Searched other than Minimum Documentation to the extent that such Documents are included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
A	EP, A, 0303292 (ASAHI GLASS CO.) 15 February 1989 ---	
A	GB, A, 1126554 (DU PONT) 5 September 1968 ---	
A	US, A, 3418302 (R.A. DARBY) 24 December 1968 -----	
<p>¹⁰ Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
25th September 1990	17. 10. 90	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	 	

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

US 9003151

SA 38074

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 05/10/90. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

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		JP-A- 1131215	24-05-89
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